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AEC RESEARCH AND DEVELOPMENT REPORT

QUARTERLY REPORT, OCTOBER THROUGH DECEMBER, 1952

CHEMICAL RESEARCH

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I. SUMMARY

In Uranium Recovery Process Studies it was shown that fission product activity is scrubbed appreciably slower than uranium, e.g., the half-time for cerium removal is about five times of that for uranium. In batch studies, 30% TBP extracted slightly more rare earths and ruthenium than did 12.5% TBP, under conditions which gave the same percentage uranium saturation. Rare earths were readily scrubbed in either case, whereas ruthenium scrubbing offered a decontamination factor of three in both cases. In Mini Studies, the 30% TBP flowsheet resulted in a better decontaminated RCU than did the 12.5%. These latter results are interpreted to mean that with the 30% TBP flowsheet, a longer hold-up time of the organic phase (lower RCX flow rate, relative to the 12.5% flowsheet) permitted more efficient scrubbing. Tests continued to show that extraction from highly acidic aqueous phases (feeds adjusted to ca. 6.0 M H^+) gives considerable improvement in decontamination. The data suggest that under these conditions and with three to four scrubs, wastes as young as six months could be processed. Pretreatment of feeds under normal acid conditions with hydrogen peroxide results in an improvement in the ruthenium decontamination factor of about two.

Distribution coefficient measurements of potential impurities (sodium, aluminum and iron) showed that these elements should not contaminate the product streams with the flowsheets now being used, in either the Uranium Recovery Process or the Redox Process.

Experiments performed in Mini's indicated that a Purex Second Plutonium Cycle with reflux not only should give a concentrated product but should also give substantial added decontamination.

Both Minis and one inch diameter pulse columns were used to demonstrate the Recuplex Process when employing plant streams. The HTU's obtained for plutonium transfer were approximately equal to those observed earlier for uranium transfer. Added decontamination is achieved, as anticipated. Higher throughputs were possible in the pulse column utilizing plates coated on one side with fluorothene.

Studies were initiated to determine the effect on solvent extraction of different dissolving conditions. Of the tests made so far, the standard Bismuth Phosphate or Redox dissolving conditions appear to be optimum.

Extraction of uranium(VI) and plutonium(IV) from hydrochloric acid solutions by 30% TBP-CCl_4 is feasible if the hydrochloric acid concentration is above 8 M. However, niobium is also readily extracted under these conditions.

Treatment of uranium product streams with certain mercaptans, followed by passage of the stream through a silica gel column, resulted in ruthenium decontamination factors as high as several hundred. Additional studies of the precipitation of the BAL-silver complex suggested that the ruthenium decontamination could be improved by the addition of nitrite suppressors.

Precipitation of uranyl peroxide followed by calcination to UO_3 gave appreciable separation from all known impurities. Although some decontamination from fission products was noted, activities of the solutions employed were too low to measure this value.

[redacted]

A solvent extraction flowsheet for nitric acid recovery was proposed and tested. Decontamination factors of a few hundred were obtained. Separation from chloride was achieved.

Activity coefficients of TBP in cyclohexane were measured by the freezing point depression method over the range up to 2.408 molal TBP. Measurement of the activity coefficient of the uranyl nitrate-TBP complex was begun. Measurement of the solubility of TBP in water from TBP-diluent solutions showed expected correlations with the molecular structure of the diluent. A preliminary value of 5.6×10^{-6} cm^2/sec has been obtained for the self diffusion coefficient of TBP in a 0.53 molal (*ca.* 10% by volume) TBP in cyclohexane.

Correlation of dispersion time, concentration of TBP, degree of equilibrium of transferring species, temperature, and frequency of stirring are presented. These data show that the vibrational dispersion test is a qualitative measurement of the energy required to obtain a dispersion.

A study of plutonium distribution with various organic phosphates, phosphonates, phosphinates and phosphine oxides show that the same dependencies on molecular weight of ester, class of compound, etc. exist as was found for uranium and nitric acid distribution.

In studies on the resin column, a gas free elution cycle was obtained when employing a batch of Dowex-50, 20-50 mesh, 8% cross linkage. (In subsequent experiments with different batches of Dowex-50, 20-50 mesh, 8% cross linkage, some of the runs were accompanied with gassing during the elution cycle). Although it is recommended that this grade of Dowex-50 (which is the commercial grade) be employed in plant application, it is also recommended that any batch of resin be tested in a laboratory column for elution cycle performance before loading a plant column with it.

Cerium(III) fluoride is being studied as a stand-in for plutonium(III) fluoride, preparatory to studying the reduction of plutonium(III) fluoride, prepared by Freonation, by calcium. Under proper conditions, cerium yields of $>$95% can be obtained. The freezing point diagram of the system; CaF_2-CaI_2, has been semiquantitatively determined.

The effect of a number of decontaminating agents on the $BiPO_4$ waste system was investigated. Only one cleaning agent, Hilco, had any detrimental effect on adsorption of fission products and plutonium by soil. Only Versene and tartrate increased the desorption of fission products and only tartrate increased significantly the desorption of plutonium.

Zirconium and niobium are extracted from nitric acid solutions with 0.1 *M* tributyl phosphine oxide (TBPO) in carbon tetrachloride. Water did not strip these fission products at all readily, whereas hydrofluoric acid removed $>$99% in two stripping stages. Plutonium(IV) is also strongly extracted by this solvent.

Iodine present in Purex solutions is readily extracted by TBP-hydrocarbon solvents. Data obtained in a study of this system indicate (1) TBP dissolves I_2, KI and HI, but not iodates, (2) Amsco 125-90W dissolves I_2, but not compounds of iodide or iodate, (3) TBP-Amsco 125-90W shows all the solution properties toward iodine compounds characteristic of either component, (4) Amsco 125-90W reacts with iodine to form iodo-organic compounds, (5) iodine dissolved in (not reacted with) TBP-Amsco

125-90W is readily removed by water or alkaline aqueous washes, and (6) TBP appears to complex iodine in some oxidation state above zero (perhaps +1). Treatment of solvent containing radioactive iodine with inert KI-I_2 helped in decontaminating the solvent from radioactive iodine. Some benefit was obtained by pre-treating the solvent with inert KI-I_2.

II. PROCESS DEVELOPMENT (H. H. Hopkins, Jr, Problem Leader)

A. URANIUM RECOVERY PROCESS

Since the Uranium Recovery Plant encountered occasional difficulties in decontaminating uranium from six year AMW (aged metal waste) during start-up, several investigations were started to understand and improve on the erratic behavior. The rate of scrubbing of fission products from the organic was studied, as this slow step limits decontamination. The effect on decontamination of using 30% TBP was investigated since this solvent composition was adopted to insure stable column operation. The effect of fluoride in the scrub as a partitioning agent was examined, in the event iron carry-over would result in high impurity content.

Work continued on methods of providing single cycle decontamination of wastes considerably younger, i.e., as young as six months. A batch countercurrent run tested further the favorable effect of extracting from a high acid system (HW-26104) and defined the required number of scrub stages as three. Pretreatment of RAF with peroxide is shown to improve ruthenium decontamination by factors of about two.

1. Decontamination of Uranium from Aged Metal Waste (H. C. Carney, E. E. Voiland)

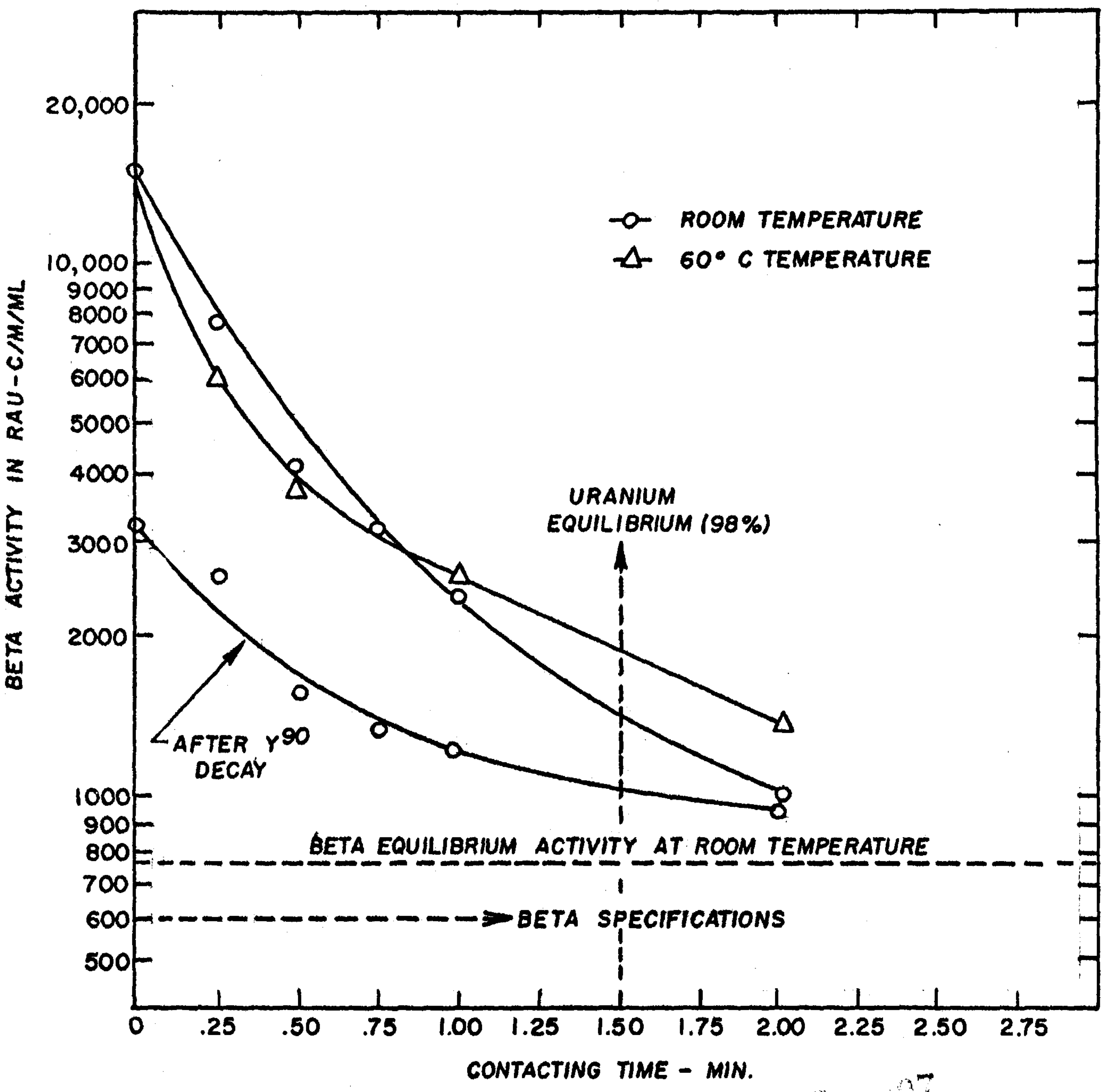
a. Rate of Scrubbing of Fission Products

Decontamination obtainable in countercurrent scrubbing was shown to be a function of residence time in the contacter, in this case a Mini (HW-25166). This result has been tested in a pulsing perforated plate contacter, designed and operated to simulate dispersion in a pulse column scrub section. Figure 1 shows the rate of scrubbing of fission products from an organic phase of RAU composition. Fission products were introduced in the organic by contacting it with RAF from six year aged waste. No great difference is found in the rate of scrubbing at a higher temperature. The top two curves represent gross beta

FIGURE I

EFFECT OF TEMPERATURE ON RATE OF DECONTAMINATION IN RA COLUMN SCRUB SECTION

SIMULATED WITH PERFORATED PLATE
STIRRER – PULSING RATE 40 RPM
ACTIVITY FROM CONTACT WITH RAF (6 YEAR AGED WASTE)



activity, including short-lived Y^{90}. The bottom curve represents long lived beta emitters (cerium) and shows that cerium is scrubbed relatively slowly, with a half time of ca. 0.5 minute (uranium half time ca. 0.1 minute).

Figure 2 shows the case where the organic has been contacted with dissolver solution. The time to scrub half the initial activity is 0.6 minutes for beta and 1.1 minute for gamma. Thus considerable difficulty is predicted for pulse column scrubbing of RAU from young wastes.

These data point to a batch mixer settler scrubber as the contacter which will supply sufficient contact time.

b. Effect of 30% TBP on Decontamination

Since 30% TBP was shown to improve RA column stability, this concentration was proposed for the RAX, such that the same TBP flow would result. The effect of this change on decontamination (as compared to that of 12.5% TBP) was tested.

Batch tests (Table 1) showed the effect over one extraction step and over one scrub step.

Although both concentrations easily produced a product RAU well within specifications, the 30% TBP extracted more activity than 12.5%, due to rare earths and ruthenium. The rare earths are readily scrubbed from organic of either concentration, but the same ruthenium decontamination factor of three is obtained in each case. Thus with younger feeds, (containing more ruthenium activity) ruthenium decontamination will be more of a problem with 30% TBP.

Essentially no cesium or strontium extract with either concentration.

Mini runs were performed comparing 12.5% and 30% TBP (Table II).

The 30% flowsheet TBP resulted in a better decontaminated RCU than did the 12.5%, a seeming contradiction of the batch results. Thus decontamination depends on the contacter used and the flowsheet. With the 30% TBP in the

FIGURE 2

EFFECT OF SCRUB RESIDENCE TIME ON DECONTAMINATION IN RA COLUMN SCRUB SECTION

SIMULATED WITH PERFORATED PLATE STIRRER
PULSING RATE 40 RPM
ACTIVITY FROM CONTACT WITH DISSOLVER SOLUTION

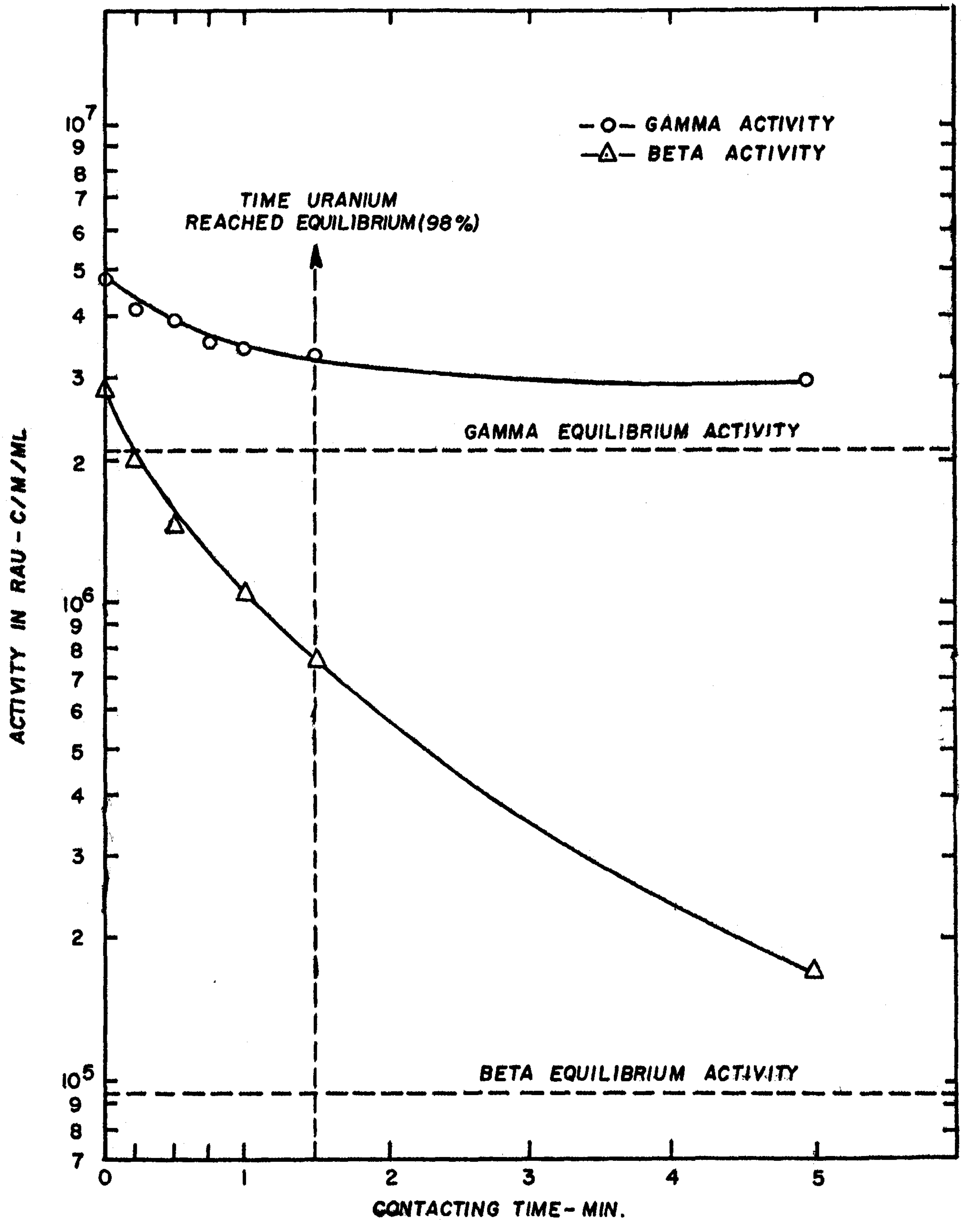


TABLE I

COMPARISON OF DECONTAMINATION BETWEEN 12.5% AND 30% TBP IN BATCH EXTRACTION-SCRUB TESTS

RAFS: from plant RAF, six year aged waste, 2.3 $\underline{M}$ H^+, 0.34 $\underline{M}$ U, $SO_4^{=}$ = $PO_4^{\equiv}$ = 0.17 $\underline{M}$, 2.7 $\underline{M}$ $NaNO_3$

RAX: TBP in Amsco
Volume ratio: $\frac{RAFS}{RAX} = \frac{1.5}{2.5}$ for 12.5% TBP

$\frac{RAFS}{RAX} = \frac{1.5}{1.05}$ for 30% TBP

Step	TBP Conc.	Activity in Organic (c/m/mg U)(1)				
		β(2)	β(3)	Ru	R.E.(4)	γ
Extraction	12.5%	105.	21.	3.5	18.	10.
	30%	170.	--	9.5	40.	23.
Scrub	12.5%	2.5	--	1.	1.	1.
	30%	4.	--	3.	1.	2.
Natural Uranium			42.			5.2

(1) Beta in BGO counter through 25 mg/cm^2 Au at 7.5% geometry
Gamma in Scintillation Counter through 1.7 g/cm^2 Pb equivalent and 10% efficiency.

(2) Counted 1 day following extraction (includes Y^{90}).

(3) Counted 25 days following extraction (corrected for UX).

(4) Counted 15 days following extraction.

TABLE II

COMPARISON OF DECONTAMINATION WITH 12.5% AND 30% TBP IN MINI RUNS

RAF: from plant, six year aged waste, 0.25 $\underline{M}$ U 3 $\underline{M}$ H^+
RAX: plant ROO (12.5%), TBP in Spraybase (30%)
Flows: HW #4, except 105 = RAX with 30% TBP, 3 Mini scrub stages, 9 Mini extraction stages.

RAX	Activity in RCU, (βc/m/mg U)(1)
12.5% TBP	31
30% TBP	12.5
Natural Uranium	72.

(1) No absorber.

Mini the organic flow is low enough so that a full scrub stage is approached closer than with the faster flowing 12.5%. This result bears out the conclusions of section (a) which pointed out the importance of a long scrub contact time.

Overall, as regards feeds of this age, it is not expected that 30% TBP will greatly alter decontamination.

c. Comparison of Plutonium Partitioning Agents

Since iron(II) introduced as a plutonium partitioning agent in the scrub presents a possible impurity problem in case of entrainment, alternate non-metallic partitioning agents were tested. Batch tests showed that 0.2 M HF resulted in plutonium distribution coefficients about 50% greater than 0.05 M Fe^{++} in the scrub. These results are close enough so that a plant test is warranted.

With no partitioning agent in the scrub, batch countercurrent runs showed an overall plutonium decontamination factor of four, whereas addition of 0.1 M H_3PO_4 to the scrub resulted in an overall factor of ten, unsatisfactorily low values.

2. Decontamination of Uranium from Current Metal Waste (H. C. Carney, E. E. Voiland)

a. Batch Countercurrent Demonstration of High Acid Extraction with Varying Scrubs (Table III).

The improvements in decontamination resulting from extraction out of a highly acidic aqueous phase and extensively scrubbing the resulting organic (cf. HW-26104) have been tested in another batch countercurrent run with CMW. The feed, adjusted to 6.0 M H^+, was processed through a manually operated mixer-settler battery consisting of three extraction, three stripping, and a variable number of scrub stages (contacters). Table III describes the run conditions and results, while Table IV presents the activities in the RCU as percentages of the activity of natural uranium. Ruthenium and niobium (to a much lesser extent) are the limiting contaminants in all cases. Rare earths, including cerium, should not be troublesome as long as two scrub stages are present. Many fission products are limiting when only one scrub stage is used.

In this demonstration using three or four scrubs and a <u>freshly</u> acidified feed, a beta decontamination factor of approximately 10^6 and a gamma decontamination factor of approximately 5×10^5 were obtained. Tests with only one, or with two scrubs were performed fifteen days later with the same feed. Comparison with the earlier run showed an improvement in decontamination factor of six by using three instead of two scrubs. This result is inconsistent with the fact that an improvement of but two is noted for the change of from one to two scrubs. The inference is that an aging process over the two week lapse of operation, results in the formation of a more extractable ruthenium species. Analysis of the RCW stream showed a beta count of 25-35% of that of the RCU. The gamma activity was perhaps one and a half that of RCU. Specific fission product analyses led to inconsistent values indicating the presence of some tightly organic-bound species, as yet unidentified.

This run, in which beta specifications were met (three to four scrubs) and gamma specifications were within a factor of three, indicates that wastes six months old could be processed under these conditions if they can be adopted to the Uranium Recovery Plant.

b. The Effect of Feed Pretreatment on Ruthenium Decontamination - Mini Runs

Batch experiments showed that treatment of RAF with hydrogen peroxide suppresses the extraction of ruthenium (HW-26104). This result, as well as the effect of nitrite, was tested in Mini runs. The conditions of pretreatment and source of feed are described in Table V. Each set of runs included a blank run, for which there was no pretreatment. The first set compared peroxide with nitrite treatment of a two year synthetic feed, the second set compared two temperatures of peroxide pretreatment, and the third set compared high acid ex-

TABLE III

U.R. PROCESS WITH HIGH ACID EXTRACTION CONDITIONS AND VARYING SCRUB STAGES

Batch Countercurrent Run #12
(Flowsheet IIB)

	Composition	Flow
RAF:	U,$PO_4^{=}$, $SO_4^{=}$, 0.15 M; H^+, 6. M; $NaNO_3$, 2.4 M	1.75
RAX:	12.5% TBP-AMSCO	2.50
RAS_1:	60% HNO_3	0.10
RAS_2:	H_2O	0.50
RCX:	HNO_3, 0.01 M	2.00

Stream In	Contactor No.	Stream Out	Contactor No.
RAX	1	RAW	1
RAF	3	RCU	5,6,7 or 8*
RAS_1	4		
RAS_2	4,5,6 or 7*	RCX	Last Stage
RCX	Last Stage		

		Activity in RCU, c/m/mg U						
		Counted Through 25 mg/cm^2 Au				Through 1.7 g/cm^2 Pb		
No. of Scrubs	Age Since Push (Days)	Gross β	Ru	Ce	TRE	Gross γ	Zr	Nb
4	95	15	10	0	0	9**	0.	20
3	95	11	11	1	0	16**	0.	18
2	110	66	72	3	1.5	54**	3.5	22
1	110	115	85	14	46	69**	25	33
RAF		$1.4x10^7$	$1.2x10^6$	$6.8x10^6$	$1.1x10^7$	$1.4x10^7$	$1.2x10^6$	$6.8x10^6$
U		42.2				1.8**		
U						5.2		

* Depends on Number of Scrub Stages Used.

** Through 8.9 g/cm^2 Pb.

TABLE IV

RCU ACITIVITY IN RUN #12 AS PER CENT OF NATURAL URANIUM ACTIVITY

	Activity in RCU (Per Cent of Natural U)						
No. of Scrubs	Beta	Ru	Ce	TRE	Gamma	Zr	Nb
3-4	30	26	2	0	500-900	0	350
2	160	190	7	4	3000	70	420
1	275	200	33	110	4000	500	630

TABLE V

FLOWSHEET AND FEED PRETREATMENT CONDITIONS FOR MINIATURE MIXER-SETTLER RUNS ON CURRENT AND ON SYNTHETIC TWO YEAR METAL WASTE

	Feed		Feed Pretreatment				
Run[2,3]	H^+ M	UNH g/l	Temperature	Time	Number of Reagent Additions	Initial H_2O_2 M	$NaNO_2$ M
HR-21	3.1	136	25°C.	---	-	--	--
HR-22	3.1	136	50°C.	2 Hrs.	1	0.3	--
HR-23	3.1	136	85°C.	3 Hrs.	1		1.0
HR-24	2.9	108	25°C.	3 Hrs.	-	--	--
HR-25	2.9	108	80°C.	3 Hrs.	2	0.4	--
HR-26	2.9	108	50°C.		2	0.4	--
HR-27	5.2	100	25°C.	---	-	--	--
HR-28	5.2	100	50°C.	2 Hrs.	2	0.6	--

1. Operating conditions for all runs were those of the HW #4 flowsheet, except for the increased feed acidity in runs HR-27 and 28.

2. Two year metal waste prepared from two year old slug was used as feed in runs HR-21, 22, and 23. Current metal waste was used as feed in runs HR-24, 25, 26, 27, and 28.

3. Runs HR-21, 24, and 27 received no feed pretreatment and served as a source of comparison.

TABLE VI

THE EFFECT OF FEED PRETREATMENT ON DECONTAMINATION AS DETERMINED BY MINIATURE MIXER-SETTLER RUNS

Run	Age Since Push	Pre-Treatment	Fission Product Activities in RAU(1), c/m/mg U						
			Beta	Ce	Rare Earths	Ru	Gamma	Zr	Nb
HR-21	2 year	(None)	86	2.0	2.6	77	45	0	1.3
HR-22	2 year	H_2O_2	24	1.5	1.8	20	14	0	6
HR-23	2 year	$NaNO_2$	57	1.0	1.4	38	30	0	---
HR-24	4 month	(None)	750	22	60	900	1950	0	---
HR-25	4 month	H_2O_2	660	20	53	660	1770	10	---
HR-26	4 month	H_2O_2	500	11	--	450	1100	26	---
HR-27	4 month	(None)	324	19	59	283	640	11	8
HR-28	4 month	H_2O_2	402	--	20	315	960	0	10

1. Beta, cerium, rare earths, and ruthenium activities were counted through a 25 mg./cm^2 gold absorber by means of a BGO (Geiger-Mueller type) counter at 7.5% geometry. Zirconium, niobium, and gamma activities were counted through a 1.7 gm/cm^2 lead absorber by means of a scintillation counter at 10% geometry.

traction conditions with and without peroxide pretreatment. From the results in Table VI, peroxide pretreatment of a two year synthetic feed is more effective than nitrite and results in an improvement of three in ruthenium, beta, and gamma decontamination factors. When applied to CMW (four months old) the better pretreatment at 50°C. reduces the ruthenium activity in the product to 50% of the value with no pretreatment. Total beta activity in the product was reduced to 67% of its former value. Further tests with high acid extraction conditions showed these to be more effective than pretreatment, and pretreatment did not improve decontamination under high acid conditions.

3. Distribution of Metal Ion Impurities

Early plant runs showed a large sodium impurity in the RCU. To elucidate this, the Chemical Research Sub-Unit undertook to measure the distribution coefficients of sodium and other metallic ions found in the Uranium Recovery Process. The phases chosen were a 12.5% TBP phase containing uranium and an aqueous scrub phase of specified composition.

A synthetic RAU (U=33 g/l) was contacted with one fifth volume portions of scrub solutions of various composition. The resulting organic solution was stripped with an approximately equal volume of 0.01 $\underline{M}$ HNO_3. UNH was added to make a standard sample (one gram uranium), and the solution was evaporated to dryness for spectrographic analysis.

There was no significant variation of the distribution coefficients for the following scrub solutions: 0.53 $\underline{M}$ ANN, 5.4 $\underline{M}$ NH_4NO_3, 2 $\underline{M}$ $Zn(NO_3)_2$, 2 $\underline{M}$ HNO_3, 6 $\underline{M}$ HNO_3 and 1 $\underline{M}$ UNH. The iron concentration (Fe^{+++} or Fe^{++}) was 0.05 $\underline{M}$, and sodium about 0.2 $\underline{M}$ in all scrub solutions. The effect of complexing agents represented by 0.2 $\underline{M}$ HF and 0.1 $\underline{M}$ Versene seemed negligible in experiments with scrubs to which these agents were added.

The distribution of sodium in the extraction step was determined by tracer experiments with Na^{24}. A synthetic RAF (containing radiosodium) with increased UNH concentration to simulate feed plate conditions was contacted with 12.5% TBP-Amsco. The resulting solutions were sampled and counted on the Gamma Scintillation Counter.

The composite results are listed in Table VII.

On the basis of these results, 4 ppm of sodium and 30 ppm iron could be found in the RCU attributable to equilibrium distribution.

B. REDOX PROCESS - DISTRIBUTION OF METAL ION IMPURITIES (E. E. Voiland)

Contamination of plant 3EU by excessive amounts of sodium was recognized early in the quarter. The Chemical Research Sub-Unit undertook to measure the distribution coefficients of sodium and of other metallic impurities (iron, aluminum) in the Redox third cycle system.

TABLE VII

METAL ION DISTRIBUTION COEFFICIENTS - 12.5% TBP SYSTEM

Aqueous Phase: (Indicated in text)
Organic Phase: 12.5% TBP in AMSCO, 0.14 M U
Phase Ratio: $\frac{\text{Organic}}{\text{Aqueous}} = 5$

A. Scrubbing Experiments

Element:	Na	Al	Fe	Zn
E_a^o:	.002-.004	$<$0.001	$<$=0.0003	0.0001
g/l aq. phase	4-9	14	2.8	130

B. Extraction Experiments

Element:	Na
E_a^o:	$<$0.001
g/l aq. phase	62

1. Measurement of Distribution Coefficients

A synthetic 3DU ($U = 114$ g/l) was contacted with various scrub solutions in the ratio of eleven volumes of organic to one aqueous. The resulting hexone phases were evaporated to dryness for spectrographic analysis. In parallel experiments, samples were taken for analysis by an alternate method. Another series of experiments utilized radiosodium, prepared by activation at Hanford. A 3DFS solution was prepared, spiked with radiosodium, and extracted with hexone. The resulting organic solution was scrubbed with different aqueous phases, and the results reported in Table VIII.

The results in Table VIII agree in order of magnitude for similar experiments analyzed by different methods.

Aluminum distributions were similar for all aqueous phases tested. Iron distributions showed little variation, although ferrous iron in the presence of acid deficient aluminum nitrate showed greater extractability.

Since zinc nitrate has been mentioned as an alternate salting agent, the distribution of zinc between 2 $\underline{M}$ $Zn(NO_3)_2$, and hexone 0.48 $\underline{M}$ U was obtained as part of these experiments. The distribution E_a°(Zn) was 0.0008.

On the basis of the distributions in Table VIII the impurity content of the 3DU (based on three water scrubs) would be 1 ppm of sodium (assuming sodium source in the aluminum nitrate at 0.3 g/l), and less than one ppm of aluminum, in agreement with plant results with the 3D column employing water scrub.

2. Effect of Uranium on Sodium Distributions

Distributions of sodium in Table VIII show an apparent dependence on sodium concentration. To clarify this effect, 2 $\underline{M}$ $NaNO_3$ was contacted with 50 ml of hexone containing no uranium. A distribution coefficient of 0.0004 was measured, as compared with 0.004 in the case of hexone containing uranium. Thus a uranium dependence is found.

TABLE VIII

METAL ION DISTRIBUTIONS BETWEEN HEXONE AND AQUEOUS PHASES

Organic: Hexone, 0.48 M U, except as noted
Aqueous: As specified

Aqueous Composition	Volume org/aq	Sodium			Aluminum			Iron		
		g/l Aqueous	$E_a^{\circ(1)}$	$E_a^{\circ(2)}$	g/l Aqueous	$E_a^{\circ(1)}$	$E_a^{\circ(2)}$	g/l	$E_a^{\circ(1)}$	$E_a^{\circ(2)}$
1.8 M ANN, 0.2 M NaOH, 0.05 M $Fe(NH_4)_2(SO_4)_2$	4	4.6	0.04	0.03	2.8	0.0015	<0.0007	49	0.0005	0.0008
1.8 M ANN, 0.2 M NaOH, 0.05 M $Fe(NO_3)_3$	4	4.6	0.04	0.03	2.8	<0.0003	<0.0007	49	0.0004	<0.0007
1. M UNH, 0.18 M $NaNO_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$	4	4.1	0.03	0.01	2.8	0.0003	<0.0007			
1. M UNH, 0.18 M $NaNO_3$, 0.05 M $Fe(NO_3)_3$	4	4.1	0.03	0.01	2.8	0.0003	<0.0007			
5.4 M NH_4NO_3, 0.18 M $NaNO_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$	4	4.1	0.02		2.8	0.0003				
5.4 M NH_4NO_3, 0.18 M $NaNO_3$, 0.05 M $Fe(NO_3)_3$	4	4.1	0.02		2.8	0.0003				
2 M $NaNO_3$	4	46	>0.002	0.005						
2 M $NaNO_3$	4	46	$0.0004^{(3)}$							
1.0 M UNH, 1.8 M ANN, 0.2 M NaOH	2	6	$0.01^{(4)}$							
1.8 M ANN, 0.2 M NaOH	4	4.6	$0.02^{(4)}$							
1.8 M ANN, 0.2 M NaOH	4	4.6	$0.0003^{(3)(4)}$							
1.2 M UNH	11	0.5	$0.008^{(4)}$							

(1) Analyses by spectrochemical methods.
(2) Na analyses by flame photometer, Al and Fe colorimetrically.
(3) No U in either phase.
(4) Radiosodium tracer technique. Hexone initially 0.23 M U.

The variation of $E_a^\circ(Na)$ with uranium concentration was studied over a range of uranium and acid concentrations. $E_a^\circ(Na)$ was found to increase with increasing uranium concentration and decrease with increasing acidity. For an aqueous phase of 0.8 M ANN and 0.2 M NaOH the distribution coefficient can be represented by $E_a^\circ(Na) = .0002 + .0002[U]$ where $[U]$ represents the uranium concentration in g/l in the aqueous phase. This expression holds over a range of 5-80 g/l uranium in the aqueous phase.

The apparent dependence of $E_a^\circ(Na)$ on sodium concentration observed in Table VIII, can be explained by assuming the sodium extracted is independent of the aqueous phase sodium concentration and is fixed by other conditions.

3. Effect of Non-Volatile Oil

In addition to these experiments using redistilled hexone as solvent, scrub studies were made using plant 0-2 Hexone (Batch 137) and hexone containing 1% non-volatile oil which was supplied by Chemical Development. No significant differences in the distribution coefficients for sodium and aluminum were observed from those given in Table VIII.

C. PUREX PROCESS-SECOND PLUTONIUM CYCLE EMPLOYING REFLUX (W. H. Adams, H. C. Carney, H. H. Hopkins, Jr., E. E. Voiland)

The study of the second plutonium cycle employing reflux, a study which was initiated last quarter with batch countercurrent runs in separatory funnels, was resumed with continuous countercurrent testing in the Mini (miniature mixer settler). The feed for this run was ORNL IBP. Due to the age of the feeds, (240 days) the purposes of the run were to measure overall decontamination factors (as well as the activity level of the final product) and to test the flowsheet as to stability, waste losses, and product concentration.

The final most successful conditions of operation are described in Table IX. These conditions were employed in the final eight hours of the total of 52 hours of operation. During the initial hours of operation hydrostatic difficulties in Mini operation and choice of poor flow rates necessitated frequent changes

TABLE IX

PUREX SECOND Pu CYCLE REFLUX RUN #5

Feed Source: ORNL IBP from runs HCP 6-1, 7-2, 8-1, 8-2, 9-1, 9-2
Extractant: 30% TBP in Amsco, carbonate treated

Final Conditions

Relative Flow	Rate ml/min	Stream	Composition
100	6.3	2AF	6 M HNO_3, 0.05 M NO_2^-, 0.2 g/l Pu(1)
20	1.29	2AX	30% TBP in Amsco
6	0.37	$2AS_2$	6 M HNO_3
12.7	0.78	$2AS_1$	Nominal 60 g/l Pu
13	0.80	2BX	0.2 M H_2SO_4
0.3	0.021	2BP	Nominal 60 g/l Pu

Mini Extraction Sections	12.	
Mini Scrub Sections	6	(1 with 2AS, 5 with 2AS, + $2AS_2$)
Mini Strip Sections	12	

Typical End Stream Analyses (g/l Pu)

Time	2 AW	2 BW	2 BP
14-1800	0.0008	0.0005	44.
15-0500	0.0007	0.002	21.
15-1100	0.0022	0.0025	42.
16-1500	0.0006	0.001	55.
17-0300	0.0032(1)	-	45.
17-0500	0.002(1)	0.0006	--
17-0700	0.0016(1)	-	64.
17-0800	0.004(1)	0.0015	58.

(1) Analysis of last two feed batches showed 6.5% and 22% Pu (VI).

in operating conditions to keep the plutonium profile from shifting strongly either towards the waste aqueous, or towards the waste organic. The scrub was initially 3 M HNO_3, but by changing to 6 M HNO_3, the scrub flow rate was found to be a convenient control variable under conditions of Table IX. An increase in this flow shifts the plutonium profile past the scrub into the strip unit, while a decrease will shift the profile back into the extraction section.

Startup was effected with nitric acid as feed, until steady flow of all streams was assured. Concentrated plutonium solution was spiked into the scrub stages until the estimated holdup had been added, then feed was admitted.

Upon attempting to use 0.1 M HNO_3 as stripping agent, the operators promptly encountered hydroxide precipitation in the strip section, followed by plugging of passages and overflow, necessitating complete shutdown. Use of sulfuric acid was then resumed.

Table IX includes typical end stream data, excluding the period in which precipitation occurred. Table X describes the decontamination obtained in the run. This decontamination was measured in the last hours of running, with the most active feed. These decontamination factors are very encouraging, but the results cannot be regarded as final due to the age of the feeds (ca. 240 days).

TABLE X

DECONTAMINATION IN PUREX SECOND Pu CYCLE REFLUX RUN #5

Feed Activity:

	Activity in 10^5 c/m/mg Pu				
Source	(1) β	Ce	Ru	(2) γ	Zr-Nb
HCP 8-2	16	7	6	730	24
HCP 8-1	18	3	12	2100	840

Product Activity:

	Activity	
Time	βc/m/mg Pu	γc/m/mg Pu
16-1000	950	1150
16-1400	910	1030
17-0300	910	1220
17-0700	870	1110

Average Decontamination Factor: β: 8×10^3 (sp. act. of Pu = 700 c/m/mg Pu)
γ: 3×10^5 (sp. act. of Pu = 700 c/m/mg Pu)

(1) β counts on BGO, 25 mg/cm^2 Au
(2) γ counts in Scintillation Counter at 1.7 g/cm^2 Pb

Thus the second plutonium cycle with reflux can produce a concentrated product (<u>ca.</u> 60 g/l Pu) and provide good decontamination (<u>ca.</u> $10^4 \beta$, $10^5 \gamma$). Further work should employ young feeds and test the separation from UX.

D. RECUPLEX PROCESS

1. Mini Demonstrations (W. H. Adams, H. C. Carney, H. H. Hopkins, Jr., E. E. Voiland, P. K. York)

Work was undertaken by the Chemical Research Sub-Unit to demonstrate the Recuplex processes in its dual Mini. This work was undertaken with cooperation of the 234-5 Development group, who agreed to supply feeds for the Mini and pulse column runs.

The aims of the Mini program were (1) to demonstrate low waste losses, (2) to demonstrate high product concentration, and (3) to uncover any serious chemical difficulty inherent in an extended run. Two flowsheets were tested, one to extract plutonium from dilute recovery streams (Flowsheet HW #8), and one to extract plutonium from a mixture of concentrated main line feeds and recovery streams (Flowsheet HW #9).

Four runs were performed. The first run, 1023-1025, demonstrated the recovery of plutonium from low concentration feeds, and defined the required ratio of strip to solvent. The second run, 1105-1107, demonstrated recovery from more concentrated solutions (4.6 g/l Pu feed) and defined the necessary extractant-feed ratio to provide low waste losses when using a feed containing a fair fraction of plutonium(VI)(<u>ca.</u> 50%). The third run 1119, demonstrated a revised flowsheet for recovery from the more concentrated solutions when the feed contains mostly plutonium(IV). Equilibrium curves were obtained. The fourth run showed that a feed containing mostly plutonium(VI) would require an excessively large number of stages or more solvent due to its lower distribution.

a. Demonstration of Dilute Flowsheet (Type HW #8)

The flowsheet composition of the feed CAF is as follows:

	M
Al^{+++}	0.45
AlF_3	0.04
Ca^{++}	0.1
Fe^{+++}	0.002
H^+	3.8
Mg^{++}	1.3
NO_3^-	7.9
Pu	0.3 g/l

Feed was received from the 234-5 Development group and the run was performed as indicated in Table XI. Startup was accomplished in the usual manner, i.e., running feed a short time, then loading the contactor with plutonium from a concentrated solution until the estimated holdup was in the system, then admitting the feed again. Physically, the system operated fairly well, except that the organic from the extraction section occasionally came over in large slugs, instead of dripping smoothly.

TABLE XI

RECUPLEX MINI RUN 1022-1024 (Type HW #8)

Final Conditions

Relative Volumes	Flow ml/min	Streams	Composition
100	5.	CAF	0.45 M Al^{+++}, 0.214 g/l Pu (70% IV), etc.
44	2.2	CAX	15% TBP in CCl_4
20	0.1	CCX	0.2 M HNO_3
1	0.05	CCP	Nominal 21 g/l Pu
19	0.95	CAS	Nominal 21 g/l Pu

16 Mini Extraction Sections
2 Mini Scrub Sections
12 Mini Strip Sections

Average End Stream Analyses Under Above Conditions:

AW	0.001 g/l Pu	(0.6%)
CW	0.007 g/l Pu	(0.7%)
CP	18. g/l Pu	

The aqueous was returned to the extraction unit as scrub by means of an air lift. Product removal utilized a Milton Roy Mini Pump, at low stroke, operated periodically by an interval timer.

The original flowsheet called for a strip flow less than that finally used. It was found for this contactor that the ratio of extractant to strip must be less than 2.4. Also the original flowsheet called for an acidity of 0.12 M, whereas 0.2 M was used. The former was not tried in view of the disastrous results in the Purex run (Section C).

The average analyses presented in Table XI show that overall operation was satisfactory. Individual analyses obtained during the run showed many wide deviations from the averages, and are not presented here.

Samples were obtained from the settling chambers after shutdown. Operating lines were plotted, but could not be determined for the concentrated ends, due to interstage flow in the Mini after shutdown. Equilibrium values were determined and are presented in Figure 3. The low concentration stripping values were inaccurate due to insufficient contact time and are not presented here.

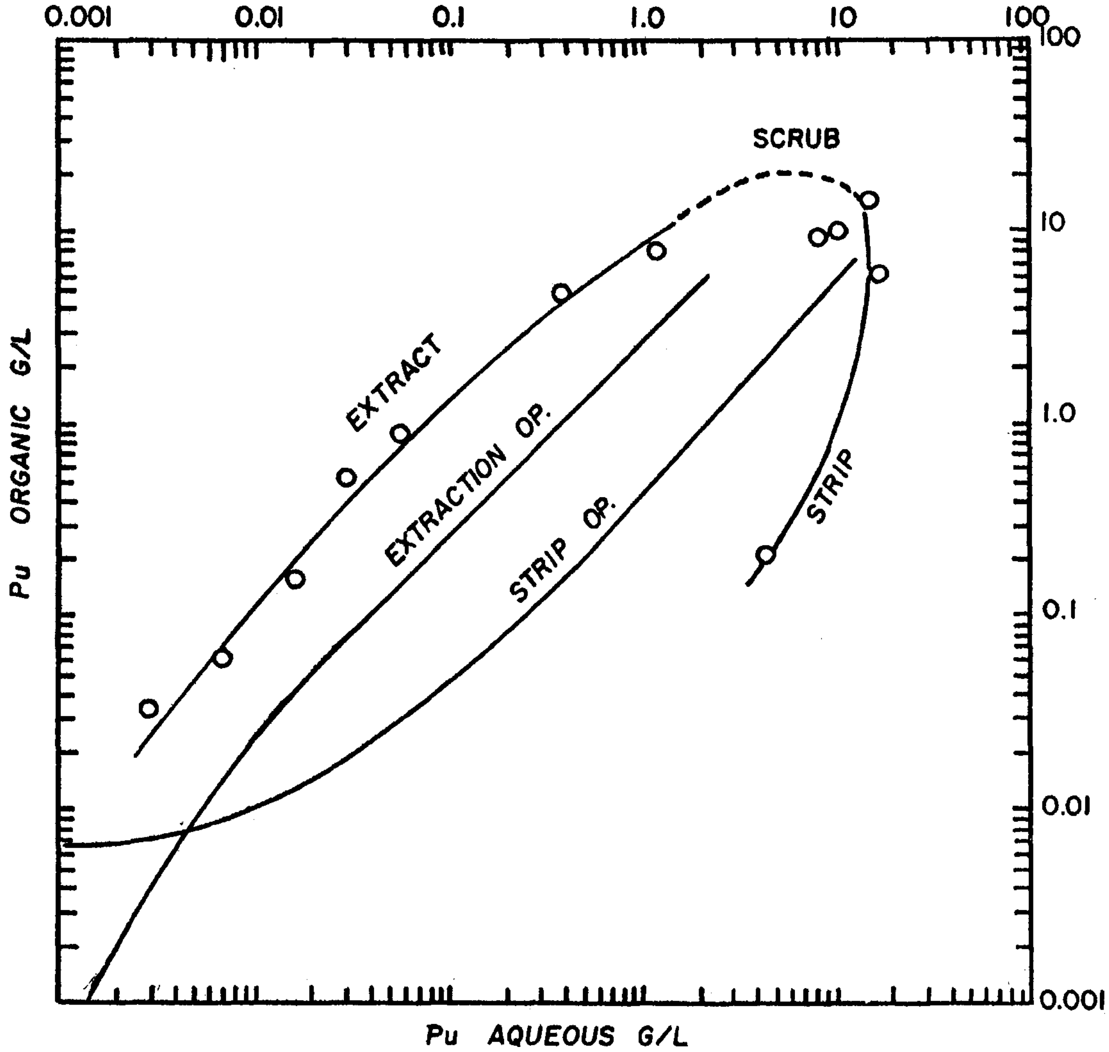
b. First Demonstration of Flowsheet Type HW #9, Mini Run 1105-1107

Flowsheet HW #9 describes the extraction of plutonium from a concentrated solution, 4.6 g/l Pu. Feed for this demonstration run was received from the 234-5 Development group and introduced into the Mini after loading the Mini with plutonium as before. Operation proceeded smoothly due to hydraulic improvements to the Mini setup. Twenty-nine hours of operation included two periods of five hour operation with no change of variable.

FIGURE 3

RECUPLEX RUN 1022-1024

PLUTONIUM EQUILIBRIUM AND OPERATING LINES



CAX: 15 % TBP IN CCl_4

CAFS: Al^{+++} 0.38 M
H^+ 3.2 M
Mg^{++} 1.0 M
NO_3^- 6.6 M
Pu 0.2 G/L

Feed Composition (CAF) for flowsheet HW #9 is as follows:

Al^{+++}	0.45 M
AlF_3	0.02
Ca^{++}	0.05
Fe^{+++}	0.001
H^+	4.0
K^+	0.02
La^{+++}	0.09
Mg^{++}	0.7
NO_3^-	7.1
Pu	4.6 g/l

TABLE XII

RECUPLEX MINI RUN 1105-1107 TYPE HW #9

Final Conditions

Relative Volumes	Flow ml/min	Stream	Composition
100	3.2	CAF	4.3 g/l Pu (56% IV), 0.4 M ANN, etc.
150	4.8	CAX	15% TBP in CCl_4
68	2.2	CCX	0.2 M HNO_3
5	0.16	CCP	Nominal 83 g/l Pu, 0.6 M HNO_3
63	2.04	CAS	Nominal 83 g/l Pu, Reflux

16 Mini Extraction Sections
1 Mini Scrub Section
11 Mini Strip Sections

Representative Endstream Analyses (g/l Pu)

Time	CAW	CCW	CCP
11-6 - 1000	0.0005	0.0010	63.
11-7 - 0300	0.002	0.0016	71.
0400	0.001	0.0019	67.
0500	0.001	0.0012	70.
0600	0.003	0.0008	59.
0700	0.002	0.0007	64.

The feed used in this run was of slightly different composition from that described above, and those differences are given in Table XII. Final conditions of the run are included. The flow conditions were altered from the flowsheet values (CAF = 100, CAX = 50) in order to reduce aqueous waste losses from 0.05 g/l Pu to 0.002 g/l Pu. The change was required by the high percentage of plutonium(VI) in the feed (44%), necessitating increasing the extractant flow.

The equilibrium curve was obtained by equilibrating samples of both phases from the stages for five minutes. This curve is presented with the calculated operating line, Figure 4.

This run, 1105-1107, demonstrated that low extraction and stripping losses can be maintained, although at an increased extractant flow. A product concentration of ca. 65 g/l Pu was reached.

c. Demonstration of Flowsheet HW #9B, Mini Run 1119

This flowsheet was designed with increased salting strength to enable operation at the designed flow ratio of one half volume extractant per volume feed. These flows are presented with other data concerning run 1119 in Table XIII. Since no long term adverse effects had been found in previous runs this run was limited to nine hours duration.

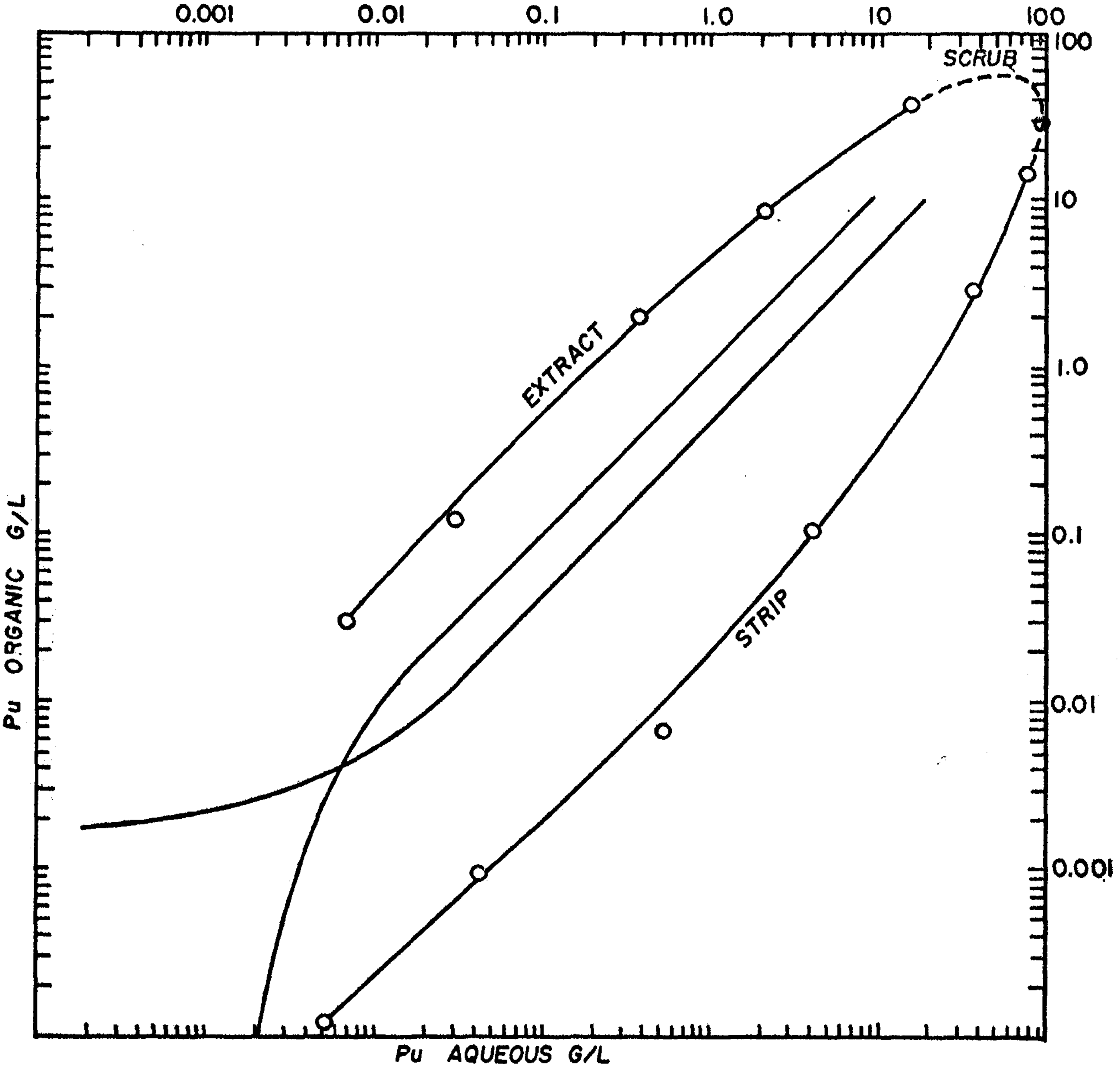
Feed for the run was prepared by the 234-5 Development group and was treated with peroxide to reduce plutonium(VI) before shipment. Startup was made with no product takeoff until the proper amount of plutonium was in the system. Operation appeared satisfactory, although the orange brown color of plutonium(VI) could be seen building up in the middle extraction stages. High waste losses were observed in the middle of the run, but these steadily decreased, so were due to some transient effect.

Stage samples were withdrawn and equilibrated, resulting in the equilibrium curve shown in Figure 5. Individual samples were analyzed for plutonium(IV) and plutonium(VI), resulting in the equilibrium curves of Figures 6 and 7. The plutonium(IV) curve includes points obtained from batch contactings of a feed of the same CAF concentration as specified by HW #9, but containing only 0.007 g/l Pu, treated to insure the (IV) state. The plutonium(VI) curve includes

FIGURE 4

RECUPLEX RUN 1105 - 1107
FLOWSHEET NO. 9

PLUTONIUM EQUILIBRIUM AND OPERATING LINES



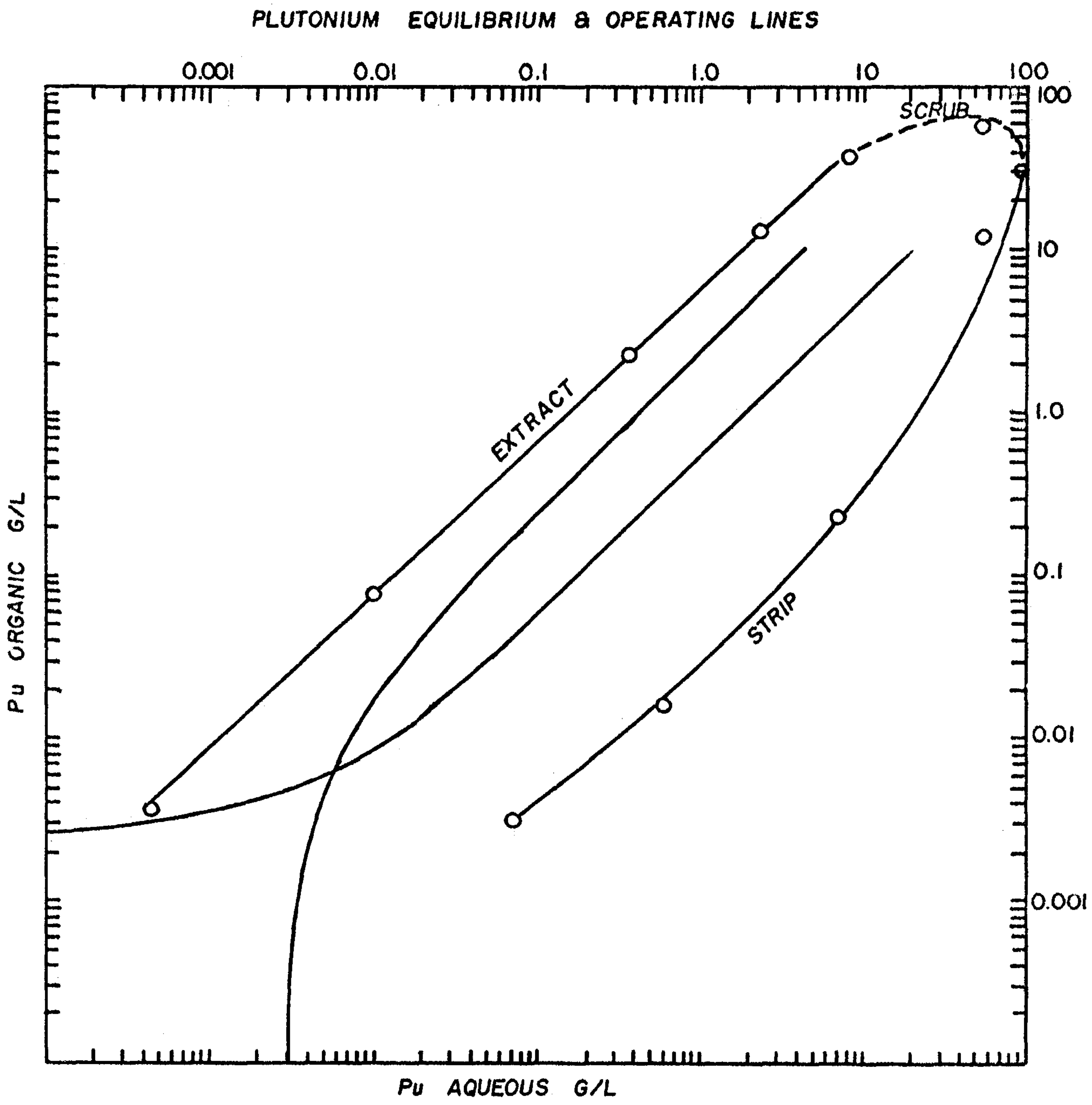
CAX: 15 % TBP - CCL_4

CAFS AL^{+++} .25 <u>M</u>
H^+ 2.5 <u>M</u>
NO_3^- 4.3 <u>M</u>
ETC.

FIGURE 5

RECUPLEX RUN 1119

FLOWSHEET NO. 9B



CAX: 15% TBP - CCl_4

CAFS: Al^{+++} $\overset{M}{.42}$

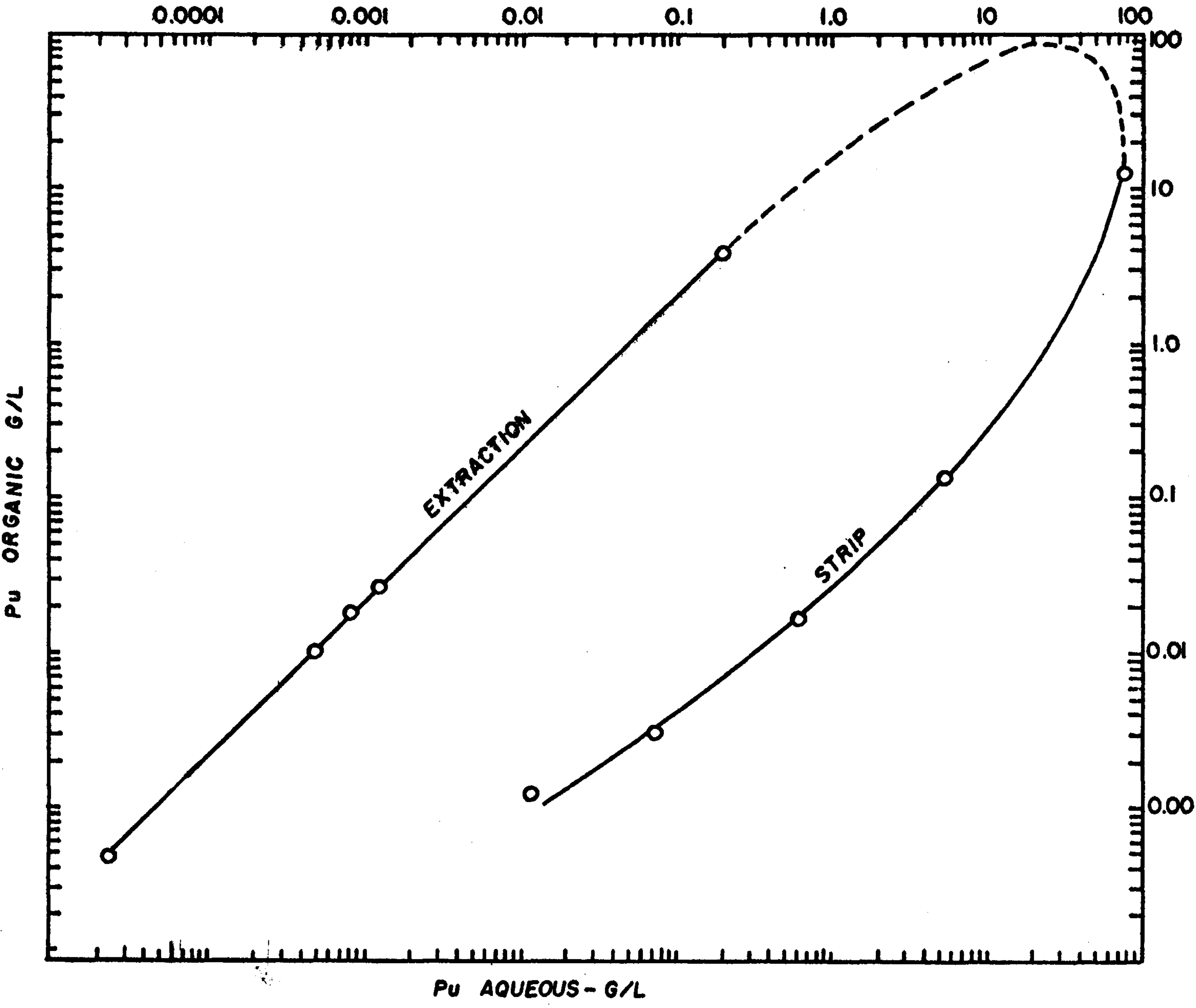
H^+ 3.3

NO_3^- 5.9

ETC.

FIGURE 6

PLUTONIUM EQUILIBRIUM LINE
Pu IV
FLOWSHEET NO. 9B CONDITIONS



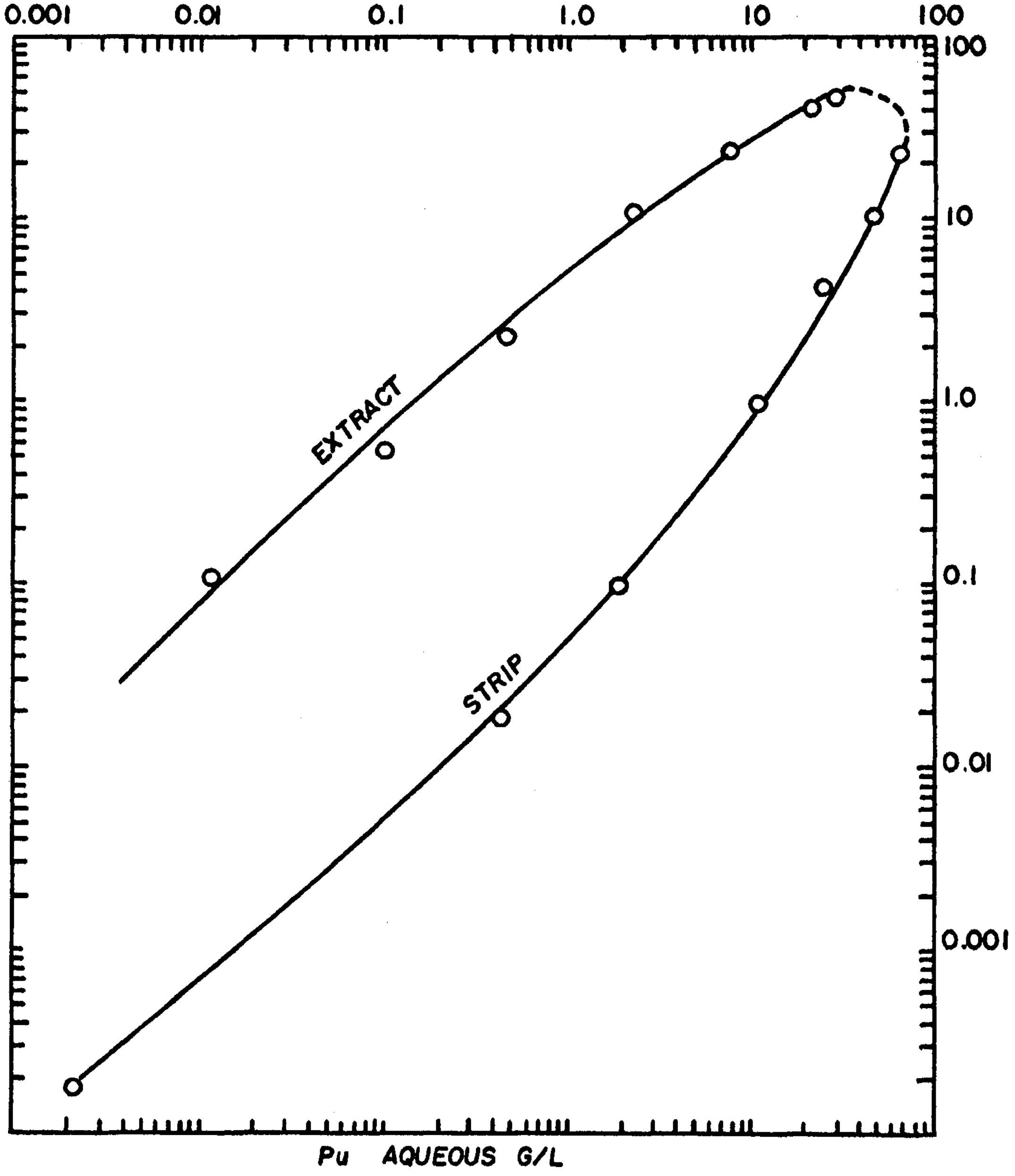
CAX: 15% TBP - CCl_4

		M
CAFS:	Al	0.42
	H^+	3.3
	NO_3^-	5.9

ETC.

FIGURE 7

PLUTONIUM EQUILIBRIUM LINE
87% Pu VI
FLOWSHEET NO. 9B CONDITIONS



CAX: 15% TBP - C Cl_4

CAFS: Al^{+++} $\overset{M}{0.42}$
H^+ 3.3
NO_3^- 5.9
ETC.

TABLE XIII

RECUPLEX MINI RUN 1119, FLOWSHEET HW #9B

Final Conditions

Nominal Relative Volumes	Flow ml/min	Stream	Composition
100	3.2	CAF	0.49 M ANN (nominal), 4.0 g/l Pu (79% IV), 3.5 M HNO_3, etc.
56	1.8	CAX	15% TBP in CCl_4
28	0.9	CCX	0.2 M HNO_3
5	0.16	CCP	80 g/l Pu (nominal)
23	0.74	CAS	80 g/l Pu (nominal)

16 Mini Extraction Sections
1 Mini Scrub Sections
11 Mini Strip Sections

End Stream Analyses (g/l Pu)

Time	CAW	CCW	CCP
1119 0010	0.009	0.015	63.
0200	0.08	0.006	83.
0300	0.06	0.055	77.
0400	0.007	0.005	78.
0500	0.004	0.002	80.
0630	0.002	0.003	84.

points obtained from special runs using feed containing plutonium predominantly in the VI state. The plutonium(VI) curve lies a factor of three below the (IV) curve in the extraction section. Thus pretreatment of the feed, (as with peroxide) is desirable to insure conversion to plutonium(IV).

d. Demonstration of Flowsheet HW #9B with Pu(VI)

Short Mini runs were performed with a feed containing plutonium predominanatly in the VI state prepared by adding oxidized plutonium solutions to slag and crucible solution. The purpose of these runs was to obtain an equilibrium curve and observe overall performance.

Although the feed analyzed 4.6 g/l Pu (85% VI) and flowsheet flows were followed, the product could not be refluxed to 83 g/l in four hours due to high aqueous waste losses (0.8 g/l Pu). The organic losses were low (0.003 g/l Pu). Thus Flowsheet HW #9B will fail with high percentages of plutonium(VI) present, unless a large number of extraction stages are provided.

The run was repeated with a very low reflux ratio, in order to obtain dilute plutonium(VI) equilibrium points. All points are plotted in Figure 5. The low concentration stripping points are subject to considerable error.

2. Pulse Column Studies (W. S. Figg, O. H. Koski)

In order to provide data for plant design beyond that available from separatory funnel, Mini-Mixer-Settler, and cold (uranium vice plutonium) pulse column studies, a series of runs with plutonium has been made in the one inch i.d. glass pulse columns located in the multi-curie wing of the 222-S Building.

a. Summary and Conclusions

The results of the seven runs and the pertinent equipment specifications are summarized in Table XIV. The conclusions drawn from these data may be outlined as follows:

(1) Flowsheets HW #8A (dilute feed) and HW #9B (concentrated feed) were shown to be operable in the pulse columns. However, since specification waste losses could not be reached with the column heights available, the dilute regions were studied in simple column runs.

(2) The H.T.U.'s obtained for plutonium transfer were found to be approximately equal to those obtained for uranium in a similar study with synthetic feeds (HW-24377).

(3) Because of unfavorable equilibrium conditions afforded by plutonium in the (VI) state and because of the ease with which feeds may be reduced

to less than 5% plutonium(VI) by hydrogen peroxide treatment, all feeds used were >95% plutonium(IV).

(4) Flowsheet HW #9B, as demonstrated in run No. 7, provided an overall beta decontamination factor of 15 and an overall gamma decontamination factor of 48.

(5) At the pulse conditions of these runs, 0.75 in at 50 cyc/min, when using all steel plates the A column was found to flood at 500 gal/hr/sq. ft. and operated with precarious stability at 350 gal/hr/sq. ft. Addition of fluorothene coatings to the upper sides of the plates provided stable operation at 800 gal/hr/sq. ft. Higher throughputs are apparently feasible with coated plates.

b. Discussion

One of the important objectives of these runs was the determination of the relative heights of uranium and plutonium transfer units for Recuplex pulse column systems in order to increase confidence in the column specifications as given in HW-22734. The above statement that plutonium and uranium transfer heights were found to be approximately equal is based on Flowsheet 12A (uranium vice plutonium) runs by Swift (HW-24377) made under conditions of column geometry and pulse which were essentially identical to those of the present runs.

Uranium was added to the A column feed in several of the runs reported here and the end streams were analyzed as shown in Table XIV. When the necessary equilibrium data are obtained, uranium transfer unit heights will be calculated for these runs. These results will provide a direct comparison in the same run.

The usual trend of decreasing transfer unit heights with increasing concentration of the transferring material is evident in the results.

The large increase in column throughput rates that is made available by the use of fluorothene coated plates in the Recuplex A column was first

TABLE XIV

1-IN. I.D. PULSE COLUMN RUNS RECUPLEX FLOWSHEETS DATA SUMMARY

Run No.	1	2	3	4	5	6	7
Flowsheet No.	8A	8B	9B	9B	9B	9B	9B
Volume Velocity: gal/hr/sq. ft. (sum of both phases)							
Extraction Section	350	315	250	800	800	800	800
Stripping Column	180	165	130	420	420	420	420
Stream Compositions, g/l Pu							
CAF	0.060	0.390	0.0075	0.0075	0.0075	4.6	4.6
CAW	0.005	0.025	0.00014	0.00010	0.00011	0.043	0.75
CAP (CCF)	0.90	9.1	0.030	0.016	0.016	8.4	29.3
CCP (CAS)	0.87	26.7	0.037	0.033	0.026	13.3	61.2
CCW	0.0019	0.0035	0.00025	0.00019	0.00020	0.011	0.10
Stream Compositions, g/l U							
CAF	0.46	--	--	--	0.0075	4.6	--
CAW	0.0040	--	--	--	0.00016	Not Determined	--
CAP (CCF)	15	--	--	--	--		--
CCP (CAS)	20	--	--	--	0.12		--
CCW	0.058	--	--	--	0.0023		--
Run Type	Reflux	Reflux	No Reflux	No Reflux	No Reflux	No Reflux	Reflux
Continuous Phase in A Column	Aqueous	Aqueous	Aqueous	Organic	Organic	Organic	Organic
Continuous Phase in C Column	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous
Extraction Section Efficiencies, Pu							
Number of Transfer Units	2.7	2.9	4.3	5.0	4.8	5.0	5.6
H.T.U., feet	1.34	1.26	1.08	0.94	0.98	0.63	0.64
Number of Stages	1.14	1.07	1.76	2.2	2.0	2.2	2.4
H.E.T.S., feet	3.2	3.0	2.64	2.1	2.3	2.1	1.5
C Column Efficiencies, Pu							
Number of Transfer Units	6.7	8.6	5.1	6.3	5.0	7.4	9.8
H.T.U., feet	0.69	0.54	0.90	0.74	0.94	0.63	0.46
Number of Stages	2.3	3.2	1.90	2.20	1.62	3.4	3.8
H.E.T.S. feet	2.0	1.45	2.46	2.12	1.87	1.36	1.24
Type of Plates*	Steel	Steel	Steel	Coated	Coated	Coated	Coated

*Plates indicated as "Steel" were all stainless steel; plates indicated as "Coated" were coated on the upper surface with two 0.003-in. thick layers of fluorothene, fused "Kel-F Dispersion".

TABLE XIV (CON'T)

Column Specifications

Plate Spacing	1-in.
Plate Hole Size	0.04 in.
Plate Open Area	23%
Column i.d.	1-in.
Extraction Section	
Length	
Simple Runs	56-in.
Reflux Runs	44-in.
Scrub Section Length	12-in.
Stripping Sect. Length	56-in.
Disengaging Sects., i.d.	2-in.
Disengaging Sects., Length	6-in.

Pulse Conditions

A Column
  Amplitude 0.75-in
  Frequency 50 cyc./min.
C Column
  Amplitude 0.375-in
  Frequency 100 cyc./min.

observed in the above mentioned cold uranium studies. These observations have been confirmed by the present runs. In general coated plates seem to provide their greatest throughput enhancement in those systems that are restricted to low volume velocities by small phase density differences and/or large emulsification tendency. For example, in Recuplex C column operation, which is characterized by high phase density difference and unusually rapid separation of phases, a much less pronounced effect of plate coating has been observed.

The gamma decontamination afforded by the Recuplex process is important both in respect to avoidance of build-up of activity in recycled solvent, and with respect to the potential radiation hazards in subsequent processing steps.

Decontamination measurements made in Run No. 7 are tabulated below:

	ARITHMETIC D.F.
Gross Beta	15
Gross Gamma	48
Ruthenium	>20

Additional analyses to be determined are Zr-Nb decontamination and fission product contamination of the extractant.

III. PROCESS IMPROVEMENT (R. L. Moore, Problem Leader)

A. FISSION PRODUCT BEHAVIOR AS A FUNCTION OF DISSOLVING CONDITIONS

(W. W. Schulz, R. A. Watts)

A study of the effect of changes in the conditions of the conventional nitric acid dissolving on the subsequent solvent extraction behavior of fission products has been initiated this quarter. A knowledge of the effects produced by changes in dissolution conditions should be useful in relating solvent extraction data to dissolver solution history. The variables being investigated are the time and temperature of dissolution, the presence or absence of a metal heel, and the final acidity of the dissolver solution. Six dissolvings of uranium pellets punched from wafers cut from 60-120 day cooled Hanford slugs have been carried out. The dissolver solutions thus obtained were used in extraction-scrub studies under both Redox and Purex conditions to characterize fission product behavior.

1. Dissolving Experiments

Dissolution of the hot metal punchings was carried out in a glass vessel fitted with a removable top to permit addition of the metal pieces. Openings in the top were provided for introducing acid and water. A reflux condenser was attached during dissolution. Traps connected to the condenser served to absorb nitric oxide, nitrogen dioxide, and any ruthenium tetroxide given off during the dissolving operation. Figure 8 is a schematic drawing of the equipment used in these dissolution studies.

Normal Redox dissolving procedure calls for the dissolution (in three cuts) of 74% of an initial 7700 pound charge. Each cut requires approximately six hours and is carried out with 60% nitric acid at reflux temperatures (101 - 108°C.). Dissolving is continued until a specific gravity of 1.82 (at boiling temperature) has been attained. The resulting solution is approximately 2 M in UNH and -0.5 M to 0 M in HNO_3.

According to the Redox Technical Manual[1] "The rate of the uranium-dissolution reaction varies directly as the temperature and acid concentration. The following equations indicate the chemistry of the reactions:

$$U + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

$$U + 8HNO_3 \longrightarrow UO_2(NO_3)_2 + 6NO_2 + 4H_2O$$

Since in actual practice in the Bismuth Phosphate Plants it has been found that about 5.5 moles of acid are consumed per mole of uranium, the composite dissolution reaction at the boiling temperature, 101 to 108°C., may be expressed as:

$$U + 5.5HNO_3 \longrightarrow UO_2(NO_3)_2 + 2.25NO_2 + 1.25NO + 2.75H_2O."$$

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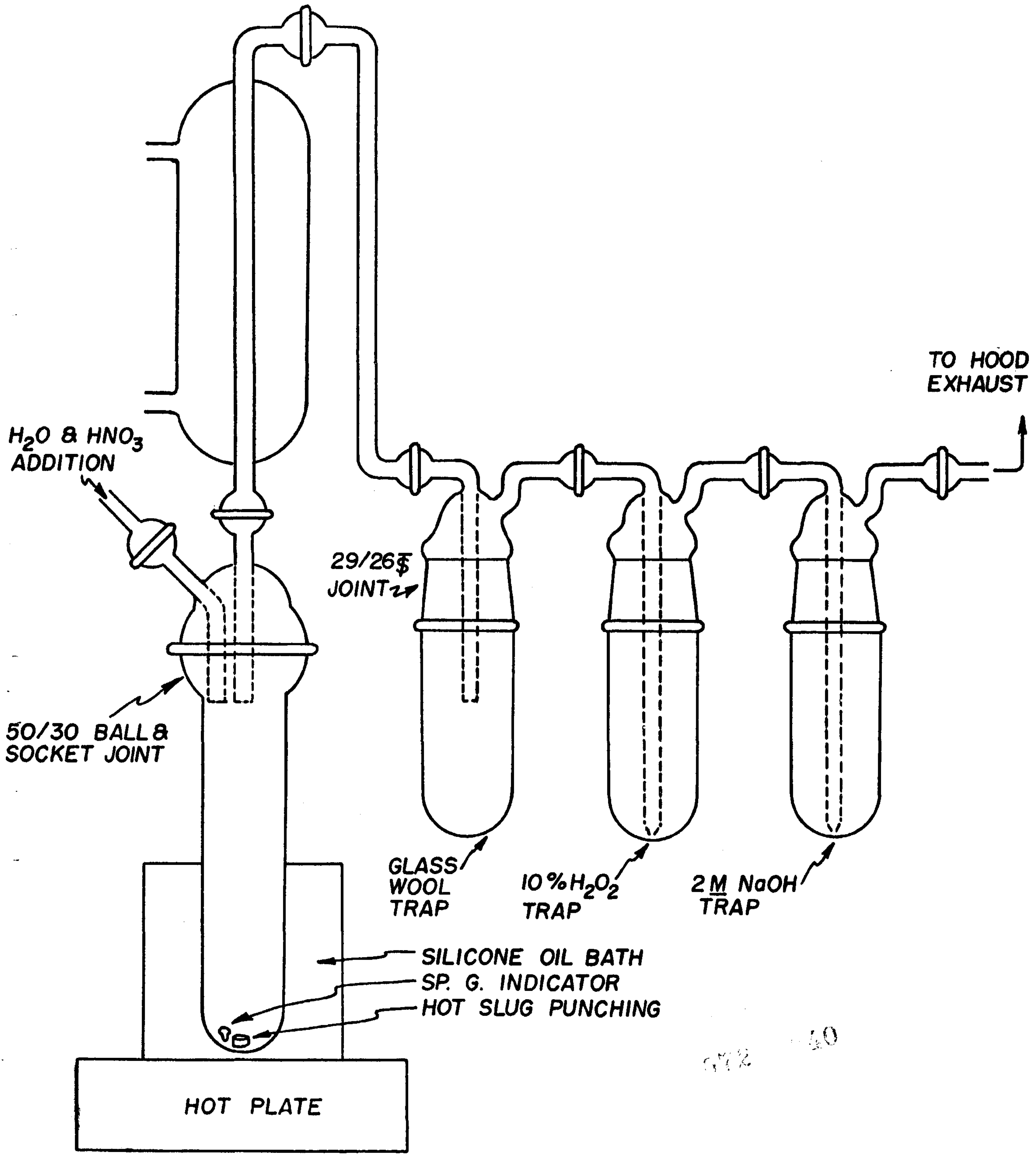
[1] HW-18700, Redox Technical Manual, July 10, 1951, p. 305.

FIGURE 8

APPARATUS FOR DISSOLUTION OF SLUG PUNCHINGS



Two dissolvings (N-1 and N-2) were made simulating the standard Redox dissolving conditions described above. These two dissolvings differed from the normal Redox procedure in that only one cut was made and the dissolving time was necessarily shorter than plant practice due to the small size of the punching. The dissolver solutions produced were not air sparged and were threfore dark in color due to the presence of dissolved NO_2. In these dissolvings and also in dissolving N-4, a small glass bubble was placed in the dissolver pot. This bubble was so constructed as to float at a specific gravity of 1.82 at boiling temperature. This device made possible simulation of Redox Plant dissolution practice described earlier.

One dissolving (N-3) was made to determine the effects on fission product behavior of complete dissolution. Complete dissolution to low acidity required approximately three times as long as dissolving to a heel.

One dissolution (N-4) was conducted simulating conditions of an abnormal Redox Plant dissolving (run number S-2-6-DR-3, June 5, 1952). Unfavorable meterological conditions during the second cut from a 7700 pound charge in this run prevented the discharge of active gases to the atmosphere. Accordingly, the dissolver solution was cooled to 55°C. and held at this temperature eleven hours before meterological conditions were again favorable. The solution was then heated to 100°C. and refluxed one hour to complete the dissolving. Adverse behavior of ruthenium in subsequent solvent extraction operations in the Redox Plant was attributed to the extended dissolution time.

In two of the dissolvings (N-5 and N-6) sufficient 60% HNO_3 was added to make the dissolver solutions 3 and 6 $\underline{M}$ HNO_3 respectively, after complete dissolution of the metal.

A complete tabulation of dissolving conditions used is given in Table XV.

TABLE XV

SUMMARY OF DISSOLUTION CONDITIONS
(60% HNO_3 Used in each Dissolving)

Dissolver Solutions Number-Type	Wt. U. Charged (g.)	Time Since Pushed (days)	% Heel	Dissolution Time (min)	Dissolution Temperature	Final UNH (M)	Final HNO_3 (M)	Moles HNO_3 Consumed per mole Uranium
N-1* Simulated Redox	12.66	75	22	90	100 - 110°C.	1.97	-.50	5.4
N-2* Simulated Redox	12.23	105	15	90	100 - 110°C.	2.05	-0.48	4.6
N-3 Complete Dissolution Low Final Acidity	8.70	82	0	300	100 - 110°C.	2.23	0.80	5.2
N-4 Long Time, Low Temp.	12.92	90	18	690 45	55 - 60°C. 100 - 110°C.	2.06	0.03	4.7
N-5 Complete Dissolution High Final Acidity	11.51	112	0	180	100 - 110°C.	1.31	3.38	5.9
N-6 Complete Dissolution High Final Acidity	4.73	124	0	150	100 - 110°C.	0.98	6.60	5.2

*Solution not air sparged after dissolving and contained dissolved NO_2. An air sparge was carried out in the remainder of the dissolvings.

2. Redox Extraction-Scrub Studies With Laboratory-Prepared Dissolver Solutions

Batch extraction-scrub studies using concentrations and volume ratios of the HW #2 Redox Flowsheet were carried out to characterize fission product behavior in the various dissolver solutions. The procedure followed in making these extraction-scrub determinations was that described in HW-22076[2].

The general technique used was as follows: A portion of the dissolver solution was oxidized by making 0.1 M in sodium dichromate and heating one hour at 95°C. The oxidized dissolver solution was adjusted to 0.2 M acid deficiency and added to an equal volume of an aqueous scrub solution with a composition simulating that of the scrub stage adjacent to the IA feed plate. This IAFS mixture was extracted with twice its volume of distilled hexone which had been previously equilibrated with an aqueous solution simulating IAFS composition in the IA extraction stage immediately below the feed plate, i.e., 1.0 M ANN, 0.2 M NaOH, 0.2 M UNH, and 0.02 M $Na_2Cr_2O_7$. Phases were intimately mixed by stirring for ten minutes. Aqueous and organic phases were disengaged by centrifugation and separated. The aqueous phase was sampled and discarded.

Scrub data were obtained by scrubbing the organic phase three times with one-fourth volume of scrub solution. Analytical samples were taken of the three aqueous scrub solutions and of the final hexone phase. It was necessary to assume 100% material balance in each step since sampling the organic phase after each scrub would not allow a sufficient volume of final solutions for radiochemical assay. All glassware, stirrers, etc. were dri-filmed to prevent adsorption of radio colloids. All apparatus contacting the active solutions was discarded after a single use to avoid cross contamination.

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[2] HW-22076, H. G. Hicks, C. G. McCormack, and W. E. Roake, "Laboratory Demonstration of Redox Feed Head-End Treatment.", July 15, 1951, pp. 29-30.

The procedure described was carried out with dissolver solutions N-1 through N-4, and also with Redox plant dissolver solution to provide a basis for comparison. Extraction-scrub studies under Redox conditions were not made with those dissolver solutions (N-5 and N-6) which were high in acidity and only 1 M in UNH. Duplicate extraction-scrub studies were made when a sufficient volume of dissolver solution was available.

Ruthenium, cerium, zirconium, and niobium were the only fission products individually determined in this investigation. Plant experience has shown that these fission products are responsible for the major part of the activity in the Redox IBU stream. Ruthenium and cerium activities were counted on the second shelf of a BGO counter through a 25 mg/cm^2 gold absorber while zirconium and niobium mounts were counted through an 8.9 g/cm^2 lead absorber in a gamma scintillation counter.

The results of these experiments are summarized in Table XVI and XVII.

As the results for dissolver solutions N-1 and N-2 show, zirconium, niobium and, to a lesser extent, ruthenium decontamination was substantially lower than that obtained with Redox plant dissolver solution. It is believed that this lower decontamination is due to the presence of dissolved NO_2 in the dissolver solutions.

In the case of solutions N-3 and N-4, no significant differences from results with standard plant dissolver were noted. This indicates that complete dissolution (N-3) or extended dissolution at a low temperature (N-4) has little or no effect on fission product behavior during solvent extraction under Redox conditions. Since these solutions had been thoroughly air sparged to remove NO_2, the favorable decontamination factors obtained lend support to the idea that dissolved NO_2 is responsible for the adverse effects noted with solutions N-1 and N-2.

TABLE XVI

REDOX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

A. OVERALL DECONTAMINATION FACTORS

One extraction, three scrubs

IAF: 2.0 M UNH, -0.2 M HNO_3, 0.1 M $Na_2Cr_2O_7$

IAS: 0.04 M UNH, -0.18 M HNO_3, 2.0 M ANN

IAX: Distilled hexone pre-equilibrated with a solution of the composition 0.2 M UNH, -0.17 M HNO_3, 1.0 M ANN

Volume ratios: IAF/IAS/IAX = 1/1/4

Dissolver Solutions Number and Type	Time Since Dissolved (days)	Overall Decontamination Factors (Extraction, 3 scrubs)					
		Gross Beta	Gross Gamma	Ruthenium	Cerium	Zirconium	Niobium
Plant Dissolver Standard Redox	33	1.58×10^4	6.1×10^3	3250	------	6.06×10^4	4.22×10^4
N-1* Simulated Redox	8	9.56×10^3	276	1605	1.57×10^6	675	377
N-2* Simulated Redox	6	1.18×10^4	2.9×10^3	634	1.30×10^7	4.54×10^3	6.05×10^3
N-3** Complete Dissolution Low Final Acidity	9	2.32×10^4	1.45×10^4	1410	5.8×10^6	1.08×10^5	3.0×10^4
N-4** Long Time, Low Temp.	8	4.11×10^4	2.14×10^4	2175	------	2.25×10^4	3.1×10^4

*Dissolver solution not air sparged and dark in color.

**Decontamination factors are averages of duplicate extraction-scrub runs.

TABLE XVII

REDOX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

B. FISSION PRODUCT DISTRIBUTION COEFFICIENTS

Dissolver Solutions Number & Type	Time Since Dissolved (days)	Activity	Distribution Coefficients Extraction	Scrub 1	Scrub 2	Scrub 3
Plant Dissolver Standard Redox	33	Gross beta	0.0016	0.037	0.12	0.21
N-1* Simulated Redox	8	" "	0.0015	0.034	0.21	0.76
N-2* Simulated Redox	6	" "	0.0024	0.025	0.07	0.80
N-3** Complete Dissolution Low Final Acidity	9	" "	0.0020	0.016	0.13	0.35
N-4** Long Time, Low Temp.	8	" "	0.0013	0.013	0.10	0.56
Plant Dissolver	33	Gross gamma	0.0026	0.062	0.13	0.22
N-1*	8	" "	0.0086	0.091	1.50	3.90
N-2*	6	" "	0.0022	0.053	0.32	1.50
N-3**	9	" "	0.0008	0.049	0.20	0.52
N-4**	8	" "	0.0013	0.017	0.21	0.83

TABLE XVII (CON'T.)

REDOX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

B. FISSION PRODUCT DISTRIBUTION COEFFICIENTS

Dissolver Solutions Number & Type	Time Since Dissolved (days)	Activity	Distribution Coefficients			
			Extraction	Scrub 1	Scrub 2	Scrub 3
Plant Dissolver	33	Ruthenium	0.011	0.063	0.093	0.085
N-1*	8	" "	0.018	0.071	0.16	0.30
N-2*	6	" "	0.009	0.078	0.30	0.79
N-3**	9	" "	0.010	0.044	0.13	0.38
N-4**	8	" "	0.004	0.056	0.20	0.59
Plant Dissolver	33	Cerium	------	------	-----	----
N-1*	8	" "	0.0007	0.0027	0.010	0.86
N-2*	6	" "	0.0009	0.0022	0.004	0.11
N-3**	9	" "	0.0006	0.0020	0.053	0.25
N-4**	8	" "	------	------	-----	----
Plant Dissolver	33	Zirconium	0.0002	0.033	0.60	0.32
N-1*	8	" "	0.0010	0.72	6.4	33.
N-2*	6	" "	0.0010	0.058	1.5	4.8
N-3**	9	" "	0.0004	0.015	0.22	1.5
N-4**	8	" "	0.0003	0.070	0.30	1.8
Plant Dissolver	33	Niobium	0.0001	0.046	0.51	0.82
N-1*	8	" "	0.0014	4.9	19.	34.
N-2*	6	" "	0.0011	0.11	0.78	1.6
N-3**	9	" "	0.0001	0.20	0.68	0.60
N-4**	8	" "	0.0003	0.051	0.33	1.4

*Dissolver Solution not air sparged.
**Distribution coefficients are averages of duplicate extraction-scrub runs.

3. Purex Extraction-Scrub Studies With Laboratory-Prepared Dissolver Solution

Batch extraction-scrub studies with the various dissolver solutions were made using concentrations and volume ratios of the HW #1 Purex Flowsheet. Duplicate studies were carried out with each of the six dissolver solutions in the same manner as Redox experiments previously discussed. Results for these Purex studies appear in Tables XVIII and XIX.

Dissolver solution N-1, as discussed earlier, was produced using standard Redox Plant dissolving conditions. The solution, however, was not air sparged and contained dissolved NO_2. As the results in Table XVIII show, poor decontamination from ruthenium, zirconium, and niobium was obtained upon solvent extraction three days after dissolving. Solvent extraction after allowing this solution to stand an additional 10 days however, yielded results comparable to those with standard plant dissolver solution. Solvent extraction of dissolver solution N-2 (prepared in the same manner as solution N-1) four days after dissolving also gave poor decontamination factors for ruthenium, zirconium, and niobium. A fifteen minute air sparge of solution N-2 conducted after the solution had been standing a total of eight days resulted in a noticeable lessening of the dark color of the solution. Subsequent solvent extraction showed an improvement in fission product behavior as can be seen from Table XVIII.

A reasonable explanation for the improvements in fission product behavior obtained when these solutions are allowed to stand or are air sparged is to attribute the improvement to the removal of NO_2 initially present in the dissolver solution. The reason for the detrimental effect of the presence of dissolved NO_2 gas is not readily apparent. Further experimental evidence is needed to resolve the question satisfactorily.

With dissolver solutions N-3 and N-4 decontamination factors for ruthenium, zirconium, and cerium are similar to those obtained with plant solution. Poor niobium decontamination, however, was observed with both solutions. This adverse behavior of niobium is not attributable to any effects of dissolved NO_2 since both solutions were thoroughly air sparged. Rather, the extended time of dissolution used in the preparation of these solutions seems responsible for the low niobium decontamination factors. Dissolving N-4 was carried out at a lower temperature than that used in Redox plant operation, but the effect on niobium was also evident with solution N-3 where normal reflux temperatures were used. The high extraction coefficients for the second and third scrub stages with solutions N-3 and N-4 (Table XIX) indicate that a long digestion period changes the scrub behavior of niobium.

Total dissolution to a high final acidity is detrimental as the results for solutions N-5 and N-6 show in Table XVIII. In the case of solution N-5, where dissolution was carried out to a final acidity of 3.38 M, zirconium, ruthenium, and cerium decontamination factors are similar to those obtained with plant dissolver. Adverse niobium behavior was responsible for the poor overall gross gamma decontamination obtained. Even poorer niobium decontamination was obtained with solution N-6 where dissolution was carried out to a final acidity of 6.6 M. Data in Table XIX show the niobium distribution across the extraction stage to be significantly higher for solution N-6 than for the other laboratory-prepared dissolver solutions.

The short dissolution times used in preparing solutions N-5 and N-6 indicate that the poor niobium decontamination is not due to any time effect such as was observed with solutions N-3 and N-4. To insure the absence of dissolved NO_2, solutions N-5 and N-6 were thoroughly air sparged at the conclusion of the dissolution operation. This treatment indicates that NO_2 effects such as those noted with solutions N-1 and N-2 are not responsible for the adverse niobium

TABLE XVIII

PUREX EXTRACTION - SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

A. OVERALL DECONTAMINATION FACTORS
1 extraction & 3 scrubs

IAF: 1.35 M UNH, 2.0 M HNO_3, 0.02 M $NaNO_2$
IAS: 3.0 M HNO_3
IAX: 30% TBP-Amsco 125 (Carbonate and Water Washed)
Volume Ratios: IAF/IAS/IAX - 3/2/10

Dissolver Solutions Number and Type	Time Since Dissolved (Days)	Overall Decontamination Factors for One Extraction and Three Scrubs					
		Gross Beta	Gross Gamma	Ruthenium	Cerium	Zirconium	Niobium
Plant Dissolver Standard Redox	15	1.3×10^5	1.0×10^4	1.6×10^4	3.8×10^6	1.6×10^4	2.5×10^4
N-1* Simulated Redox	3 13	4.9×10^4 3.6×10^5	3.6×10^3 2.3×10^4	2.7×10^3 8.5×10^4	4.9×10^6 1.1×10^7	2.5×10^3 5.0×10^4	910 2.2×10^4
N-2* Simulated Redox	4 8**	4.6×10^4 5.4×10^4	4.1×10^3 5.3×10^3	2.7×10^3 4.2×10^3	3.4×10^7 3.7×10^6	7.0×10^3 1.1×10^4	3.2×10^3 4.6×10^3
N-3 Complete Dissolution Low Final Acidity	6	9.5×10^4	1.9×10^4	---------	6.2×10^6	2.5×10^4	7.2×10^3
N-4 Long Time, Low Temp.	7***	9.3×10^4	2.0×10^3	5.7×10^3	8.9×10^6	1.8×10^4	1.6×10^3
N-5 Complete Dissolution High Final Acidity	5*** 13	4.3×10^4 6.3×10^4	1.4×10^3 4.5×10^3	4.3×10^3 4.3×10^3	9.7×10^6	1.7×10^4 8.9×10^3	1.5×10^3 2.7×10^3
N-6 Complete Dissolution High Final Acidity	3***	3.1×10^4	730	2.3×10^3	5.2×10^6	1.4×10^4	790

*Dissolver Solution not Air Sparged
**Solution Air Sparged 15 minutes before Solvent Extraction Carried Out
***Decontamination Factors are Averages of Duplicate Extraction-Scrub Runs

TABLE XIX

PUREX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

B. FISSION PRODUCT DISTRIBUTION COEFFICIENTS

Dissolver Solutions Number and Type	Time Since Dissolved (days)	Activity	E_a^o Distribution Coefficients Extraction	Scrub 1	Scrub 2	Scrub 3
Plant Dissolver						
Standard Redox	15	Gross beta	0.0016	0.0053	0.038	0.25
N-1*, Simulated Redox	3	" "	0.0025	0.0042	0.086	0.38
N-1*, Simulated Redox	13	" "	0.0012	0.0030	0.040	0.19
N-2*, Simulated Redox	4	" "	0.0015	0.0071	0.089	0.48
N-2*, Simulated Redox	8**	" "	0.0007	0.025	0.044	0.30
N-3, Complete Dissolution						
Low Final Acidity	6	" "	0.0009	0.0047	0.11	0.49
N-4, Long Time Low Temp.	7***	" "	0.0011	0.0041	0.11	0.52
N-5, Complete Dissolution						
High Final Acidity	5***	" "	0.0020	0.0090	0.067	0.45
N-5, High Final Acidity	13	" "	0.0015	0.010	0.067	0.18
N-6, Complete Dissolution						
High Final Acidity	3***	" "	0.0016	0.016	0.075	0.22
Plant Dissolver	15	Gross gamma	0.0017	0.020	0.15	0.70
N-1*	3	" "	0.0012	0.088	0.30	0.35
N-1*	13	" "	0.0008	0.025	0.36	0.13
N-2*	4	" "	0.0012	0.048	0.39	1.0
N-2*	8**	" "	0.0071	0.0072	0.18	0.71
N-3	6	" "	0.0031	0.050	0.26	0.59
N-4	7***	" "	0.0027	0.21	1.2	2.6
N-5	5***	" "	0.0026	0.010	0.39	0.45
N-5	13	" "	0.0010	0.064	0.22	2.2
N-6	3***	" "	0.0021	0.21	0.73	1.7

TABLE XIX (CON'T.)

PUREX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

B. FISSION PRODUCT DISTRIBUTION COEFFICIENTS

Dissolver Solutions Number and Type	Time Since Dissolved (days)	Activity	E_a° Distribution Coefficients			
			Extraction	Scrub 1	Scrub 2	Scrub 3
Plant Dissolver	15	Ruthenium	0.0030	0.020	0.070	0.17
N-1*	3	" "	0.0024	0.035	0.35	0.84
N-1*	13	" "	0.0005	0.010	0.081	2.1
N-2*	4	" "	0.0031	0.045	0.19	0.49
N-2*	8**	" "	0.0037	0.034	0.12	0.28
N-3	6	" "				
N-4	7***	" "	0.0008	0.086	0.26	0.57
N-5	5***	" "	0.0070	0.028	0.10	0.20
N-5	13	" "	0.0029	0.024	0.14	1.7
N-6	3***	" "	0.012	0.039	0.076	0.15
Plant Dissolver	15	Cerium	0.0026	0.0022	0.0060	0.038
N-1*	3	" "	0.0021	0.0030	0.0052	0.090
N-1*	13	" "	0.0016	0.0010	0.0034	0.098
N-2*	4	" "	0.0010	0.0020	0.0065	0.023
N-2*	8**	" "	0.0031	0.0029	0.0036	0.043
N-3	6	" "	0.0009	0.0011	0.0054	0.33
N-4	7***	" "	0.0013	0.0011	0.0024	0.31
N-5	5***	" "	0.0023	0.0013	0.0068	0.045
N-5	13	" "				
N-6	3***	" "	0.0020	0.0010	0.0055	0.43

TABLE XIX (CON'T.)

PUREX EXTRACTION-SCRUB STUDIES WITH LABORATORY-PREPARED DISSOLVER SOLUTIONS

B. FISSION PRODUCT DISTRIBUTION COEFFICIENTS

Dissolver Solutions Number and Type	Time Since Dissolved (days)	Activity	E_a° Distribution Coefficients			
			Extraction	Scrub 1	Scrub 2	Scrub 3
Plant Dissolver	15	Zirconium	0.0025	0.014	0.016	0.060
N-1*	3	" "	0.0029	0.064	0.30	0.18
N-1*	13	" "	0.0012	0.008	0.30	0.11
N-2*	4	" "	0.0006	0.075	0.38	0.85
N-2*	8**	" "	0.0015	0.028	0.13	0.33
N-3	6	" "	0.0008	0.010	0.53	0.50
N-4	7***	" "	0.0006	0.030	0.20	0.62
N-5	5***	" "	0.0017	0.024	0.12	0.27
N-5	13	" "	0.0005	0.051	0.28	1.5
N-6	3***	" "	0.0008	0.028	0.21	0.68
Plant Dissolver****	15	Niobium	0.014	0.005	0.11	0.04
N-1*	3	" "	0.0024	0.10	1.1	0.86
N-1*	13	" "	0.0004	0.059	0.56	0.098
N-2*	4	" "	0.0006	0.14	0.77	1.4
N-2*	8**	" "	0.0006	0.060	0.55	1.1
N-3	6	" "	0.0003	0.10	0.67	1.5
N-4	7***	" "	0.0006	0.44	1.2	3.6
N-5	5***	" "	0.0012	0.37	0.39	0.43
N-5	13	" "	0.0008	0.13	0.61	0.61
N-6	3***	" "	0.020	0.40	0.53	1.08

* Dissolver solution not air sparged.

** Solution air sparged 15 minutes before solvent extraction carried out.

*** Distribution coefficients are averages of duplicate extraction-scrub runs.

****Niobium distribution coefficients with plant dissolver are in doubt.

behavior. Furthermore, in contrast to results with solution N-1, niobium behavior was not improved by allowing solution N-5 to stand thirteen (13) days before solvent extraction. The adverse niobium behavior observed with solutions N-5 and N-6 thus seems to be directly attributable to the fact that dissolution was carried out to a high final acidity in producing them.

The detrimental effect of high acidity upon niobium behavior in TBP solvent extraction has been noted earlier by Hopkins and Voiland[3]. In single batch contactings of uranium solutions prepared from low acid dissolver solution these investigators found niobium decontamination factors to be threefold lower at a feed acidity of 6.6 M than at a feed acidity of 3.6 M. The results obtained with solutions N-5 and N-6 show high acidity has an even greater effect on niobium extraction when feeds are prepared from high acid dissolver solutions.

Results with solution N-6 indicate that ruthenium decontamination was also affected by dissolution to a final acidity of 6.6 M. Although the effect on overall ruthenium decontamination is small, results in Table XIX show a significant increase in the ruthenium distribution ratio (E_a°) across the extraction stage as compared to results with plant dissolver solution.

4. Conclusions

The following statements summarize the conclusions which can be drawn from the dissolutions made to date:

a. The presence of dissolved NO_2 in both Redox and Purex IAF results in decreased decontamination from ruthenium, zirconium, and niobium.

b. Dissolution over an extended period of time appears to have an adverse effect on niobium behavior in solvent extraction under Purex conditions. The time of dissolution has no effect on fission product behavior in solvent extraction under Redox conditions.

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[3] HW-26104, Quarterly Progress Report, June-September 1952, Chemical Research Section.

c. Dissolution to a high acidity results in increased extraction of niobium and, to a lesser extent, ruthenium under Purex conditions.

5. Future Work

It is planned to extend these studies to ascertain the effects of additives during dissolution. One of the experiments envisioned will test the effect on niobium and zirconium behavior of adding phosphate ion during dissolution. Other experiments planned will test the effects of isotopic dilution caused by adding uranium-niobium and/or uranium-zirconium alloys in the dissolving operation.

B. SOLVENT EXTRACTION OF URANIUM AND PLUTONIUM FROM HYDROCHLORIC ACID SOLUTIONS (W. W. Schulz)

Results of previous investigations of the extractability of uranium, plutonium, and fission products from hydrochloric acid solutions are given in HW-26104. These results show that, whereas uranium is appreciably extracted by 30% TBP-CCl_4 from 6 $\underline{M}$ HCl, plutonium(IV) is not favorably extracted at HCl concentrations below 8 $\underline{M}$. Single batch contactings of a HCl dissolver solution also indicated radio-niobium to be readily extractable into 30% TBP-CCl_4.

In order to determine the extractability of plutonium(VI) several attempts were made to oxidize plutonium(IV) in the 6 $\underline{M}$ HCl dissolver solution to the (VI) state. The choice of oxidizing agents was limited to a very few since most oxidizing agents considered would also oxidize chloride ion to free chlorine. Among those which appeared feasible were sodium dichromate and ceric ion. With the 6 $\underline{M}$ HCl dissolver solution 0.1 $\underline{M}$ dichromate was slowly reduced to chromium (III) by chloride ion at room temperature and less than 20% of the plutonium was oxidized to plutonium(VI). Addition of 0.5 $\underline{M}$ ceric sulfate to a portion of the HCl dissolver solution produced a reddish precipitate which dissolved upon further addition of ceric sulfate. Analyses again showed less than 20% of the plutonium had been oxidized. The failure to achieve satisfactory oxidation of plutonium has resulted in not determining the extractability of plutonium(VI) from HCl solutions.

Two extraction-scrub runs were carried out with HCl dissolver solution to characterize extraction and scrub behavior of fission products. Uranium and acid concentrations were chosen at which plutonium(IV) distribution was favorable. The same general procedure as described elsewhere in this report (see page 44) was used in making these studies. Results of these runs are given in Table XX.

As is seen from the table, extremely poor decontamination was obtained in extracting uranium and plutonium from HCl solutions. Ruthenium, zirconium and, in particular, niobium exhibit poor extraction-scrub behavior.

C. REMOVAL OF RUTHENIUM ACTIVITY WITH MERCAPTANS (R. A. Watts)

1. Adsorption of Mercaptan Complexed Ruthenium Activity on Silica Gel

Work was continued this quarter on the use of mercaptans (specifically, 2,3-dimercaptopropanol-1 and β-mercaptopropionic acid) to decontaminate the Redox II DF stream. This work is also applicable to III DF or III EU solutions. II DF was used in this work because its high specific activity offers better opportunity to get meaningful analytical numbers. The specific treatment studied consists of adding the mercaptan to portions of Redox II DF solution, digesting the solution for two to three hours at 50°C. and then passing this feed through a silica gel column. A range of feed acidities was investigated with the adjustment of acidity being made after the digestion period. The results of three column runs with BAL (2,3-dimercaptopropanol-1) and one run with β-mercaptopropionic acid are presented in Tables XXI and XXII respectively.

As can be seen from the numbers reported in Table XXI for column "C", the decontamination factors for gross beta activity hold up very well over the complete range of feed acidities. The wide range of decontamination factors in columns "A" and "B" are probably a result of flow rate fluctuations. It was observed that any flow rate greater than 0.2 ml/min/ml bed gave poor decontamination factors for gross beta activity.

TABLE XX

EXTRACTION-SCRUB STUDIES WITH HYDROCHLORIC ACID DISSOLVER SOLUTION

One Extraction, Three Scrubs

IAF: 0.76 M U, HCl (Concentration as indicated)
IAS: HCl (Concentration as indicated)
IAX: 30% TBP-CCl_4 (Carbonate and water washed)
Volume Ratios: IAF/IAS/IAX = 3/2/10

IAF and IAS HCl Concentration M	Overall Decontamination Factors (Extraction-Three Scrubs)					
	Gross beta	Gross gamma	Ruthenium	Zirconium	Niobium	Total Rare Earths
6.0	2490	340	42	70	7.7	1.13×10^5
9.8	1090	130	64	28	1.7	2.00×10^4

TABLE XXI

SILICA GEL COLUMNS USING BAL-TREATED REDOX II DF SOLUTION

COLUMNS A & B

Feed Composition

UNH 2.12 M
BAL 0.05 M
gross β 1.0 x 10^6 c/m/ml (25 mg/cm^2 Au. Abs.)
gross γ 8.8 x 10^5 c/m/ml (8.9 g/cm^2 Pb. Abs.)
Ru β 1.32 x 10^5 c/m/ml (25 mg/cm^2 Au. Abs.)

Column Specifications

Bed Volume - 1 cc.
Bed Length - 19 cm.
Flow Rate - 0.2-0.3 ml/min/ml bed
Packing - Davison, grade A silica gel, 40-50 mesh

Bed Volumes (Cumulative)	Feed Acidity	Decontamination Factors				
Column A	M	gross β	gross γ	Ruthenium β	Zirconium γ	Niobium γ
17	-0.19	2.1	5.7	5	1.3	1.2
118	-0.19	3.9	7.2	19	7.1	4.6
235	-0.19	4.7	10	15	7.3	4.7
462	-0.19	26	65	18	6.8	5.1
Column B						
60	0.10	11	14	6.1	5.2	2.5
256	0.10	6.8	6.2	8.4	2.5	1.5
490	0.10	52	57	17	4.1	1.7

COLUMN C

Feed Composition

UNH 2.01 M
BAL 0.025 M
gross β 1.0 x 10^6 c/m/ml (25 mg/cm^2 Au. Abs.)
gross γ 6.1 x 10^5 c/m/ml (8.9 g/cm^2 Pb. Abs.)
Ru β 9.4 x 10^5 c/m/ml (25 mg/cm^2 Au. Abs.)

Column Specifications

Bed Volume - 2 cc.
Bed Length - 8 cm.
Flow Rate - as indicated
Packing - Davison, grade A silica gel, 40-50 mesh

Bed Volumes (Cumulative)	Flow Rate ml/min/ml bed	Feed Acidity M	Decontamination Factors				
			gross β	gross γ	Ru β	Zr γ	Nb γ
26	0.04	-0.27	21	44	216	12	1.0
47	0.05	-0.27	25	18	233	10	1.3
85	0.16	-0.27	33	21	411	4.1	1.1
173	0.25	0.30	10	10	665	3.2	1.8
250	0.21	0.30	21	19	583	4.1	2.0
283	0.19	0.30	33	28	647	4.0	2.0

TABLE XXII

SILICA GEL COLUMN USING β-MERCAPTOPROPIONIC ACID-TREATED REDOX II DF SOLUTION

Feed Composition	
UNH	2.12 M
HNO_3	0.30 M
β-mercapto-propionic acid	0.05 M

Column Specifications

Bed volume - 1 cc.
Bed length - 19 cm.
Flow rate - 0.3 ml/min/ml bed
Packing - Davison, grade A silica gel, 40-50 mesh

Bed Volumes Cumulative	Decontamination Factors				
	Gross β	Gross γ	Ruthenium β	Zirconium γ	Niobium γ
83	1.6	1.9	2.3	5.5	2.2
298	1.5	1.7	2.2	3.2	1.6
468	1.6	1.9	2.7	3.1	1.6

The feed solution for column "C" was filtered in an attempt to prevent the column plugging that had been encountered previously. This filtration step gave gross beta decontamination factors of three (3) and four (4) for the two batches of feed. The decontamination factors reported are the total decontamination factors obtained for the filtration plus the column treatment. An additional portion of Redox II DF solution was made 0.05 M in BAL and treated as above preparatory to its use as column feed. This feed was not needed and was allowed to stand several days without further treatment. At the end of this time the solution was filtered and mounted for beta and gamma counting. This filtration alone resulted in a beta decontamination factor of 130, a gamma decontamination factor of 40 and a ruthenium decontamination factor of 160. These numbers indicate that the ruthenium decontamination realized in these column runs may be due largely to the filtering action of the silica gel.

It will also be noted that the ruthenium decontamination was very good in column "C" although the BAL concentration had been lowered from 0.05 M to 0.025 M. A reduction in the BAL concentration is extremely desirable due to the presently quoted high cost of this chemical (*ca.* $70 per pound).

The run using β-mercaptopropionic acid feed treatment gave very small decontamination factors (Table XXII). However, this poor operation may have been partly due to the excessive flow rate and to mercaptan decomposition caused by feed acidification. Both mercaptans used will decompose in acid solution, although the rate is slow at room temperature and low acidity. If the mercaptan is completely destroyed before the feed is passed through the silica gel column, the ruthenium decontamination factors obtained are found to approach unity.

2. Head-End Scavenging Treatment

Previously reported results (HW-26104) indicated that Head-End scavenging of ruthenium activity with BAL or other mercaptan precipitates would depend, in part, upon the radiation stability of these compounds. Preliminary experiments with these mercaptans showed them to be very unstable when introduc into full level plant dissolver solution. It was suggested that this decomp might be due to the presence of nitrite in the dissolver solution rather tha wholly due to radiation damage. This possibility was checked by a number of experiments. Portions of simulated dissolver solution containing traces of were made 0.05 M in BAL with and without the presence of nitrite suppressors sulfamic acid, ferrous ammonium sulfate plus sulfamic acid). These cold exper ments confirmed the suspicion that nitrite was responsible, at least in part, for the decomposition of BAL in the presence of dissolver solution.

In view of this fact, several Head-End scavenging experiments with the BAL-silver complex were repeated in the presence of nitrite suppressors. The experiments were carried out with 10 ml. portions of full level Hanford dissolver solution. The precipitates showed very little visual decomposition in these experiments whereas with no suppressor the precipitate was gummy in appearance and tended to float on the surface or cling to the walls of the vessel. The results of three such runs are presented in Table XXIII.

Further experiments are planned in which the Head-End treatment will be followed by subsequent Purex solvent extraction thus testing the effects of the Head-End scavenging and the presence of excess mercaptan in the feed upon fission product behavior. Redox solvent extraction in the presence of excess of BAL is made unattractive by dichromate decomposition of BAL and subsequent emulsion formation caused by the decomposition products. However, it may be practical to remove the excess BAL (prior to dichromate addition) by use of an excess of silver or by heating.

TABLE XXIII

BAL-SILVER SCAVENGING OF DISSOLVER SOLUTION

UNH - 1.91 M
HNO_3 - 0 M
BAL - 0.05 M
Ag/ - 0.01 M

Nitrite Suppressor	Decontamination Factors		
	Gross β	Gross γ	Ruthenium
None	1.1	1.0	90
0.1 M Urea	1.0	1.0	260
0.1 M Sulfamic acid	1.2	1.0	610
0.1 M Sulfamic acid / 0.1 M Ferrous Ammonium Sulfate	1.2	1.0	770

D. PRODUCTION OF UO_3 BY CALCINATION OF URANYL PEROXIDE (R. A. Watts)

The precipitation of uranyl peroxide was investigated as a means of reducing the concentrations of ionic impurities in the UO_3 produced by the Redox and/or Metal Recovery processes. UO_4 was precipitated at room temperature from Redox plant E-12 solution (final uranium stream) diluted to a uranium concentration of ca. 0.2 M. The precipitation was carried out by the simultaneous addition of NH_4OH and H_2O_2 (the NH_4OH neutralizes the hydrogen ions produced by the peroxide reaction thereby maintaining the pH at about 2.5). The precipitated peroxide was filtered, washed, dried, and then calcined to UO_3 by heating at 250 to 300°C.

This treatment reduced the concentrations of a number of ionic impurities as shown in Table XXIV. The ions not reported in the table were well below specifications, or below the limits of spectrographic detection, before as well as after the prescribed treatment. The reactivities (for conversion to UF_4) of the UO_3 produced from UO_4 were quite good. Values of 1.25 and 1.27 were obtained for two samples as compared with values of *ca.* 0.9 for Redox-produced UO_3 and *ca.* 1.1 for Metal Recovery. The reactivity of a K-25 standard UO_3 on the same basis is estimated to be about 1.3.

Since activity was detected in the supernate obtained in the precipitation step, some fission product decontamination was expected. However, since the original solution met both beta and gamma specifications, the final activities noted in the UO_3 product were too low to permit accurate determination of any decontamination factors that might have been realized. Similarly, the calcination step produced no detectable decontamination from fission product activity.

TABLE XXIV

IONIC IMPURITIES IN UO_3 PRODUCED BY UO_4 CALCINATION

	Na*	Al*	Fe*	Li*
Original Solution	1000	200	18	10
UO_3 - 1st sample	20	50	10	<2
UO_3 - 2nd sample	50	100	10	-

*All concentrations expressed in ppm U.

E. NITRIC ACID RECOVERY PROCESS (E. E. Voiland)

If a high acid chemical flowsheet is to be considered for the uranium recovery process, some provision must be made for either the recovery or decomposition of nitric acid to render the process economically attractive. The relatively high chloride content of the RAW presents a corrosion problem in the evaporative recovery of nitric acid. However, an effective pretreatment has been proposed by L. H. Clark (HW-19105) which converts the chloride to higher valence states by oxidation with peroxysulfuric acid.

Solvent extraction is an alternate process to recover nitric acid and separate it from chloride and at least 99% of the fission products. Such a process would use RAW as feed, TBP or an anionic extraction agent with an inert diluent as the solvent. The nitric acid resulting could be directly concentrated for reuse in any first cycle plant process. For use in the uranium recovery process it could be returned directly to the feed concentrator. The aqueous waste after neutralization could be evaporated and discharged to waste with no attendant corrosion problem.

Since considerable experience with 30% TBP-Amsco was available this solvent was chosen for the first studies. A "cold" batch countercurrent run was made with simulated high acid RAW as the feed. Using the data from this run as a basis, operating diagrams were constructed and the conditions for successful recovery determined. Flowsheet AR 1 (Figure 9) was prepared and tested using an AAF prepared by acidifying 6 year old RAW with one eighth volume of 16 $\underline{M}$ HNO_3 (Table XXV). The recovered nitric acid was decontaminated from beta activity by a factor of 110 and from gamma activity by a factor of 400. Test of the product with silver nitrate solution gave no precipitate, indicating absence of chloride.

The fate of the waste uranium is at present not know, however, the possibility of recovering it with the nitric acid is good.

Further investigations will aim at increasing the beta decontamination factor to greater than 500 and determining the per cent of uranium recovery from the RAW.

TABLE XXV

ACID RECOVERY BY SOLVENT EXTRACTION

AAF: H^+, 4.6 M; $SO_4^=$, 0.15 M; $PO_4^{\equiv}$, 0.15 M; HNO_3, ~4. M;
$NaNO_3$ 2.4 M U^4, 1.1 g/l; Cl^4, 0.5 g/l.
AAX: 30% TBP-Amsco
AAS and ACX: H_2O
Flows and column makeup according to Flowsheet AR 1.

A. NITRIC ACID RECOVERY

Run No.	AAF M	AAW M	ACW M	ACP M	% out/in	% recovered
1	4.0					81
2	4.0	0.35	.03	1.48	103	86

B. DECONTAMINATION

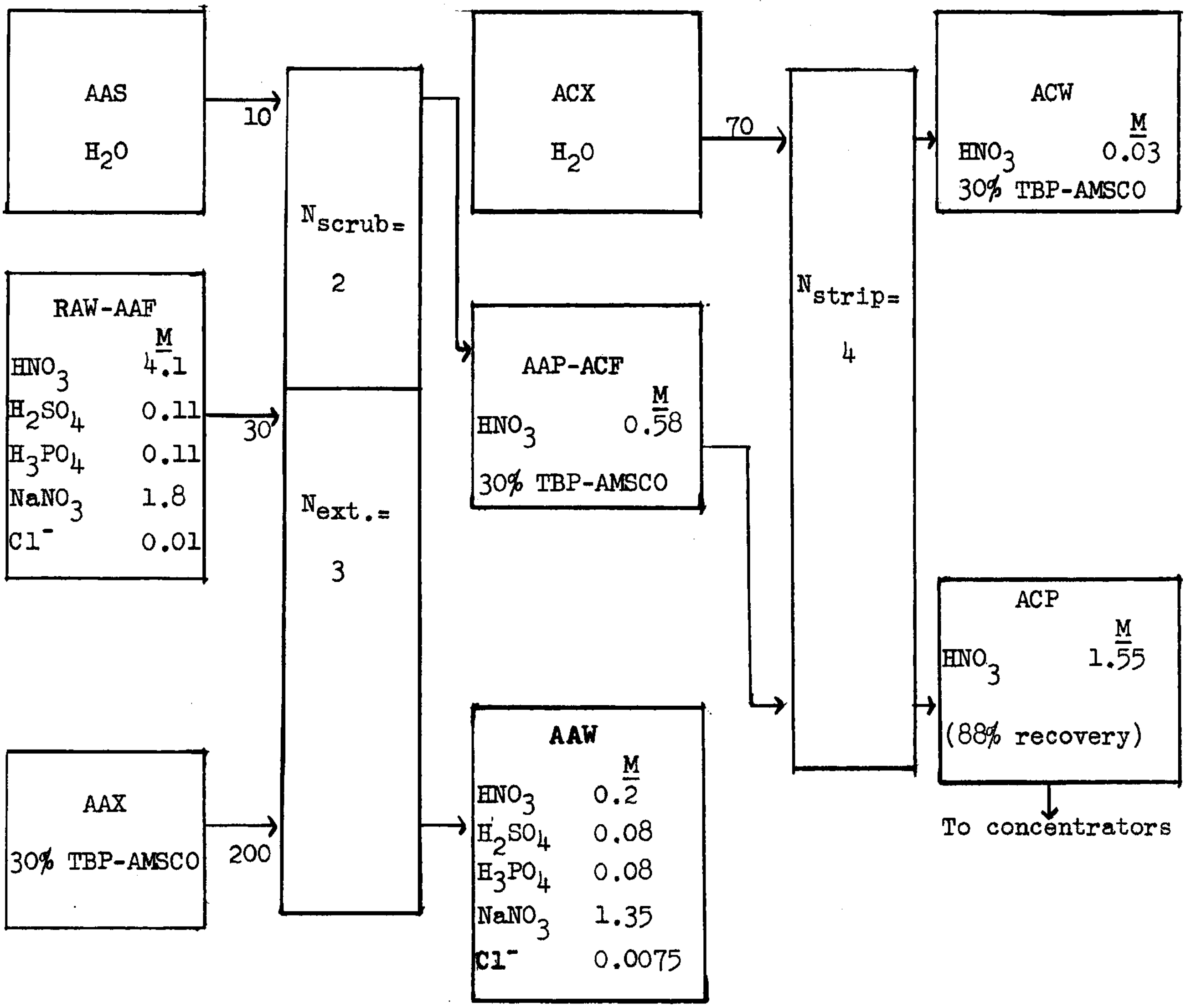
Stream	Run No.	βc/m/100g HNO_3	Date Counted	β D.F.	γc/m/100 g HNO_3	γ D.F.
AAF	1,2	2.9×10^6			2×10^6	
ACP	$1^{(1)}$	1.4×10^5	12/12		10^4	
ACP	$1^{(1)}$	0.63×10^5	12/22			
ACP	1	5.5×10^4				
ACP	2	5.73×10^4	12/16		5×10^3	400
ACP	$2^{(2)}$	3.3×10^4	12/22			
ACP	$2^{(2)}$	2.5×10^4		110		

(1) One scrub stage.
(2) Calculated value gross beta minus **yttrium** contribution.
Beta counted through no absorber on BGO, 7.5% geometry.
Gamma counted through 1.7 g/cm^2 Pb at 10% geometry.

FIGURE 9

FLOWSHEET AR 1

ACID RECOVERY BY SOLVENT EXTRACTION (30% TBP-AMSCO)



An alternative flowsheet could use, instead of the aqueous scrub, a reflux of part of the ACP. This would require an increase of ACX to maintain the same concentration factor.

Using such a reflux, a greater scrub volume could be used with probable attainment of greater decontamination.

IV. PHYSICAL CHEMISTRY OF SOLVENT EXTRACTION (L. L. Burger and W. F. Johnson, Problem Leaders)

A. ACTIVITY COEFFICIENT OF TBP IN CYCLOHEXANE SOLUTIONS (W. F. Johnson, R. L. Dillon)

The determination of the activity coefficients of TBP and uranyl nitrate-TBP complex in an organic phase was undertaken to gain a better understanding of the equilibrium involved in TBP extraction processes. Of the methods commonly employed for the determination of activity coefficients, the freezing point method was chosen because it is relatively simple, capable of high precision and the equipment was available.

Cyclohexane was chosen for the solvent as it was the only saturated hydrocarbon available in sufficient purity with a convenient freezing point. In addition it has a large molal freezing point lowering and sufficient cryoscopic data are available. The cyclohexane used was a sample of 99.1 mole per cent purity obtained from Phillips Petroleum Co. This material was given three washes with concentrated sulfuric acid, washed with water three times, dried over anhydrous sodium sulfate and distilled. The resulting cyclohexane was 99.2 mole per cent pure as determined from its freezing point. The TBP used was vacuum distilled.

Temperature was measured with a Leeds and Northrup Thermohm platinum resistance thermometer using a Mueller bridge to measure the resistance. A reciprocating double helix stirrer operated at 120 strokes per minute was used to stir the solution during the cooling and freezing process. An essentially air tight sleeve bearing made from a hypodermic syringe was placed around the stirrer shaft where it entered the top of the freezing cell to prevent moisture condensation in the sample. A uniform rate of cooling was obtained by using three concentric Dewar bottles. The inner bottle contained the sample, the outer bottle contained a dry ice-acetone freezing mixture. The inner bottle was separated from the middle bottle, which was immersed directly in the dry ice-acetone mixture, by a 1/4" air gap.

The activity of the cyclohexane was evaluated by means of the equation:

$$-\ln a_1 = (4.11 \times 10^{-3})\vartheta + (2.96 \times 10^{-6})\vartheta^2$$

The constants in the equation are based on cryoscopic data obtained from the "2" tables of the American Petroleum Institute Research Project 44[1]. Molal activity coefficients were evaluated from the activity of the solvent using the "h" function of Randall and White[2].

The freezing point lowering, and molal activity coefficients for TBP are given in Table XXVI.

TABLE XXVI

FREEZING POINT LOWERING AND MOLAL ACTIVITY COEFFICIENT AT THE FREEZING POINT FOR CYCLOHEXANE SOLUTIONS OF TBP

Molality TBP$^{(b)}$	Freezing Point Lowering, ϑ °C.	$-(\ln a_1 \times 10^3)^{(a)}$	γ_2
0.0496	0.962	3.95	0.90
0.0962	1.774	7.30	0.82
0.1306	2.407	9.91	0.79
0.1457	2.552	10.51	0.75
0.2033	3.473	14.31	0.70
0.2773	4.402	18.15	0.62
0.5079	7.360	30.40	0.50
0.8486	11.013	45.62	0.39
2.408	22.21	92.74	0.23

(a) Subscript (1) refers to cyclohexane
(b) 0.5 molal is ca. 10% by volume TBP

Heat of dilution data are not available for this system. A search of the literature for heats of dilution for a system with cyclohexane as solvent showing the large deviations from ideal such as that obtained in the TBP-cyclohexane system

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[1] American Petroleum Institute Research Project at National Bureau of Standards, Table 72, Heat and Entropy. Fusion, Freezing Points, and Cryoscopic Constants, March 31, 1947.

[2] Randall, White, J. Am. Chem. Soc., 48, 2514 (1926).

has not yielded any data which might be used to obtain an approximate value for this system. As a result it is not possible at the present time to calculate the activity coefficient at 25°C.

Preliminary data for the activity coefficient of the uranyl nitrate-TBP complex are presented in Table XXVII.

TABLE XXVII

FREEZING POINT LOWERING AND MOLAL ACTIVITY COEFFICIENT AT THE FREEZING POINT FOR CYCLOHEXANE SOLUTIONS OF URANYL NITRATE-TBP COMPLEX

Molality of Complex	Freezing Point Lowering θ °C.	$-(\ln a_1 \times 10^3)$	γ_2
0.0515	1.024	4.21	0.94
0.0956	1.845	7.59	0.88
0.1451	2.679	11.03	0.80

At present there is some uncertainty in the results for the uranyl nitrate-TBP complex caused by an uncertainty as to the amount of water present in the solutions.

Future work will be directed toward extending the concentration range for both systems and obtaining an anhydrous uranyl nitrate-TBP complex system. In addition some work is planned using n-dodecane as solvent if this can be obtained in sufficient purity.

B. THE SOLUBILITY OF TBP IN WATER FROM TBP-DILUENT SOLUTIONS (W. F. Johnson and R. L. Dillon)

The solubility of TBP in water as a function of the TBP concentration in Amsco 125-90W and carbon tetrachloride has been reported previously (HW-20936 and ORNL-1116). In the present investigation more data are being obtained for these diluents and other diluents are being studied.

The experimental technique used is essentially that described in HW-20936 using P^{32} labeled TBP except that the concentration of TBP in the organic phase after contacting is being measured by counting a sample of this phase. This latter determination is necessary inasmuch as some evaporation of the more volatile diluents occurs during equilibration with water.

The diluents which have been used thus far are Amsco 125-90W, carbon tetrachloride, benzene, n-hexane and cyclohexane. The water solubilities of TBP from these diluents are given in Table XXVIII. Solubility values listed in this table were read from smooth curves drawn through the experimental points.

TABLE XXVIII

SOLUBILITY OF TBP IN WATER FROM TBP-DILUENT SOLUTIONS

Vol. % TBP Diluent	Conc. TBP (g/l.) In Aqueous Phase					
	100	70	50	25	10	5
Amsco 125-90W	0.44	0.32	0.29	0.24	0.17	0.10
Hexane	--	0.27	0.21	0.15	0.08	0.04
Cyclohexane	--	0.23	0.16	0.11	0.08	0.05
Carbon Tetrachloride	--	0.18	0.10	0.04	0.015	0.007
Benzene	--	0.10	0.05	0.02	0.01	0.005

The data obtained for Amsco are in excellent agreement with the data for this diluent obtained previously. The data for carbon tetrachloride are in fair agreement with the lower values reported in ORNL-1116.

The data of Table XXVIII show that saturated hydrocarbon solutions of TBP have the highest water solubility of TBP, the solubility decreasing with decreasing molecular weight. Benzene solutions of TBP show the lowest water solubility of TBP as might be expected from the more acidic character of benzene. A more complete correlation of data can be made after the water concentration in the organic phase has been determined for these systems.

C. SELF DIFFUSION COEFFICIENT OF TBP IN CYCLOHEXANE

Studies of the kinetics of transfer in a two phase extraction system are greatly aided by a knowledge of the diffusion coefficients for the transferring species in the two phases. In extraction processes such as Purex or Metal Recovery in which a TBP-diluent mixture is used as the extractant the rate of diffusion of TBP is a possible rate determining step.

The method of Anderson and Saddington[1] is being used to determine the diffusion coefficient of TBP in cyclohexane using P^{32} labeled TBP as tracer. In a 0.53 molal (ca. 10% by volume) TBP in cyclohexane a value of 5.6×10^{-6} cm^2/sec. has been obtained. This low value indicates that the diffusion of TBP is a possible rate controlling step in the extraction process.

The measurement of the diffusion coefficient of TBP is being extended to other concentrations and other diluents.

D. LIQUID-LIQUID DISPERSION (R. L. Andelin, L. L. Burger)

The study of dispersion and disengaging phenomena during this period has been largely confined to TBP systems and because of the continued need for information on metal recovery extraction, the emphasis has been on the study of RAFS-RAX and similar type solutions.

The "induction time" which is a measure of the amount of energy which must be put into the system before a dispersion is produced, was discussed in the last quarterly report. An induction time is said to exist if a dispersion does not result after stirring for 15-20 seconds. It was observed at that time that this lack of dispersion was related to the transfer of bulk species from the aqueous phase to the organic phase and was influenced by temperature, the concentration of TBP and surface active agents. These variables have now been extended in both range and number. Much of the resulting information was transmitted on a day to day basis to the Chemical Development Sub-Unit which was able to make a working test of some of the results. Besides the dispersion time, the disengaging time or the time required for complete coalescence of the dispersion was also determined. A summary of these results follows:

1. Concentration Of TBP In The Diluent

TBP concentrations of 0, 5, 12 1/2, 20, 30 and 50% in Amsco 125-90W

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[1] Anderson and Saddington, J. Chem. Soc. 1949, S80, S381.

were studied with respect to dispersion and disengaging time. As the concentration of TBP is lowered the dispersion time increases and reaches a maximum in the region of 10% TBP. Table XXIX lists the results for synthetic RAFS and RAW systems and Figure 10 gives a graphic representation. Similar data have been obtained for other stirring frequencies. It will be noted that as the TBP concentration is changed, the initial dispersion time, Θ, may vary by a factor of two or more, but the disengaging time, t, is quite low and comparatively uniform. After the phases have been dispersed and separated, i.e., in chemical equilibrium, the re-dispersion time or equilibrium dispersion time, Θ_e, is relatively low and more independent of TBP concentration.

A number of tests were carried out to determine the change in dispersion time as chemical equilibrium is approached. To simulate approach to equilibrium, RAX was partially equilibrated previous to the contacting by adding UNH. Table XXX lists these data for "RAX" of different TBP concentrations. The drop in dispersion time or increased ease of dispersion as equilibrium is approached is quite apparent for the lower concentrations of TBP. It is believed that this may be of fundamental significance in the behavior of extractor apparatus. As extraction proceeds the ease of dispersion is increased leading to further dispersion which may culminate in flooding or an emulsion block in the apparatus. Concentrations of 30% TBP or higher show a somewhat safer behavior both because the ease of dispersion does not change greatly until the system reaches about 90-95% of equilibrium and because the final drop in dispersion time as chemical equilibrium is reached is smaller. The curves in Figure 11 illustrate this behavior. RAX-RAW systems, where only nitric acid is transferred, show a similar pattern but the effect is smaller in magnitude. If the organic phase contains an excess of the transferring species, either UNH or HNO_3, such that there is an initial transfer from organic to aqueous then the dispersion time is slightly lower than the equilibrium dispersion time. The process of transfer from organic

TABLE XXIX

DISPERSION AND DISENGAGING TIMES AS A FUNCTION OF TBP CONCENTRATION

Stirring frequency 60/min., Temperature 20°C.
Dispersion time, Θ, and disengaging time, t, in seconds

% TBP	RAFS(1)			RAW(2)			"RAW" Without HNO_3 (3)			H_2O		
	Θ	Θ_e^*	t	Θ	Θ_e^*	t	Θ	Θ_e^*	t	Θ	Θ_e^*	t
0	28	24	21	18	16	17	16	17	20	16	14	27
5	77	10	18	40	8	25	9	7	34	8	6	52
12 1/2	63	12	13	42	7	20	7	6	37	6	6	68
30	38	7	12	28	7	18	6	5	35	5	5	94
50	20	6	18	20	6	17	5	5	30	4	5	118

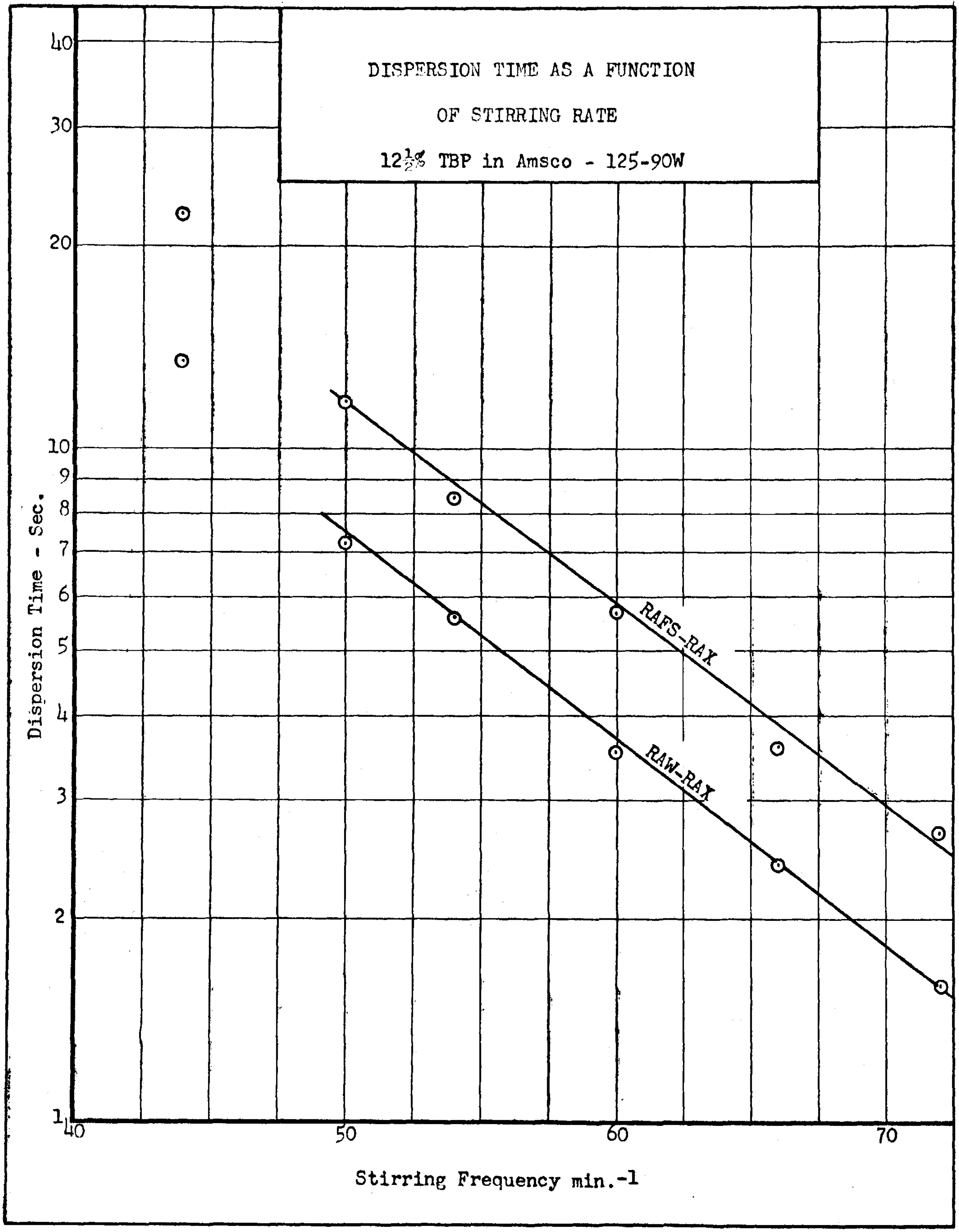
* Θ_e is the dispersion time obtained after equilibration of the phases.

(1) The composition of the synthetic RAFS was 90 g/l UNH, 27 g/l Na_2SO_4, 21 g/l NaH_2PO_4, 168 g/l $NaNO_3$, 133 g/l HNO_3

(2) The composition of the synthetic RAW was the same as RAFS without the UNH.

(3) The composition of the synthetic RAW, without HNO_3, was the same as RAFS without either the UNH or HNO_3.

FIGURE 10



DISPERSION TIME AS A FUNCTION

OF STIRRING RATE

$12\frac{1}{2}\%$ TBP in Amsco - 125-90W

TABLE XXX

CHANGE OF DISPERSION TIME AS EQUILIBRIUM IS APPROACHED

RAX + UNH contacted with RAFS
Stirring rate 44/min., Temperature = 27°C.

Per Cent of Uranium Equilibrium Initially in RAX	Dispersion Time For Different TBP Concentration in RAX				
	5%	12 1/2%	20%	30%	50%
0	210 sec.	184 sec.	131 sec.	98 sec.	48 sec.
30	180	105	124	98	48
90	130	126	118	95	47
100	← 18-25 Seconds at Equilibrium →				

to aqueous seems to favor dispersion of the organic phase, an observation which appears to be true for a wide variety of systems. For the opposite type of dispersion, i.e., organic phase continuous, no induction effect has been observed regardless of the direction of transfer.

2. Effect of Temperature

The data of Table XXXI illustrate the statement previously made that an increase in temperature lowers both the dispersion time and the disengaging time. With the RAFS-RAX system, where uranium is transferring, there is marked change with temperature, but in the absence of uranium the effect appears to be much smaller.

TABLE XXXI

CHANGE OF DISPERSION TIME AND DISENGAGING TIME WITH TEMPERATURE

System: Synthetic RAFS-RAX (12 1/2% TBP)

Temperature °C.	Dispersion Time, Θ, sec.	Disengaging Time, t, sec.
17	207	31
27	148	23
37	132	18
47	113	16

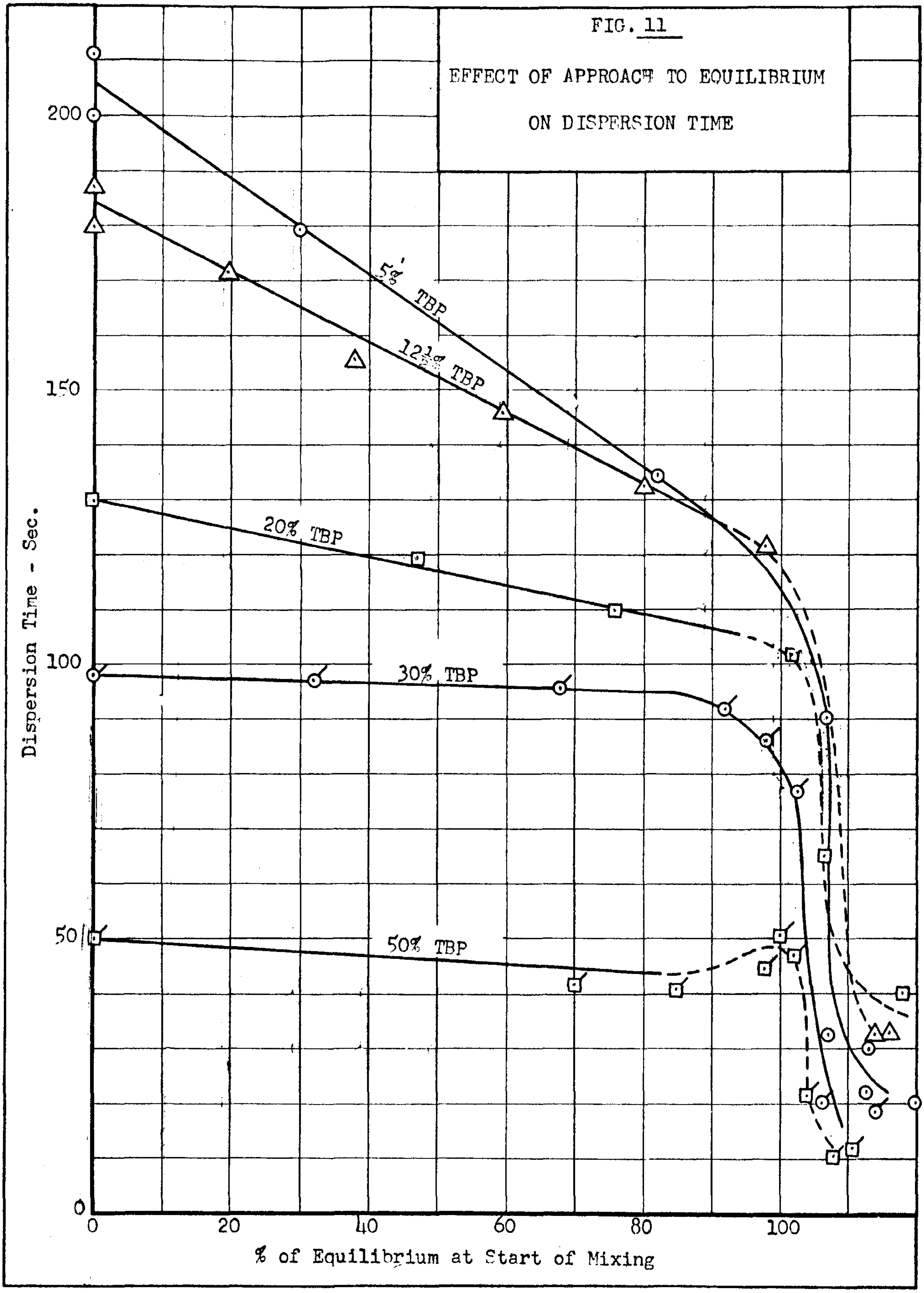


FIG. 11

EFFECT OF APPROACH TO EQUILIBRIUM ON DISPERSION TIME

The decrease in time with rising temperature is probably related to the viscosity decrease and increased diffusion rates. Attempts to make a correlation of dispersion and disengaging time with viscosity, density difference and interfacial tension will be made.

3. Frequency of Stirring

Stirring rates from 40 and 120 per minute have been used in these tests. As the energy input increases with the frequency it was of interest to examine this relation in a more quantitative manner. A minimum frequency exists for each system below which coalescence is sufficient between pulses to prevent the dispersion from building up to the reference marks on the container. As the stirring rate becomes high the character of the dispersion may change to an emulsion of very fine drops having a long disengaging time. For the systems and apparatus presently used a range of frequencies from about 40 to 75 per minute seemed to give a dispersion of similar drop size distribution. The data of Table XXXII illustrate the behavior of the Uranium Recovery extraction system for two concentrations of TBP.

TABLE XXXII

DISPERSION AND DISENGAGING TIME AS A FUNCTION OF STIRRING FREQUENCY

Temperature 27°C.

	12 1/2% TBP				30% TBP			
	RAFS-RAX		RAW-RAX		RAFS-RAX		RAW-RAX	
Freq. Φ min. $^{-1}$	Θ sec.	t sec.	Θ sec.	t sec.	Θ sec.	t sec.	Θ sec.	t sec.
44	285	8	300	9	113	7	220	9
50	137	16	88	16	70	17	60	11
54	95	23	66	17	46	22	42	12
60	65	25	44	14	40	26	34	11
66	44	32	31	15	25	32	23	13
72	32	31	21	17	18	28	14	17

It will be noted that the disengaging time for RAFS-RAX solutions changed appreciably with frequency, suggesting that the dispersion character is different. These dispersions will be examined photographically in an attempt to ascertain drop size distribution as a function of the stirring variable.

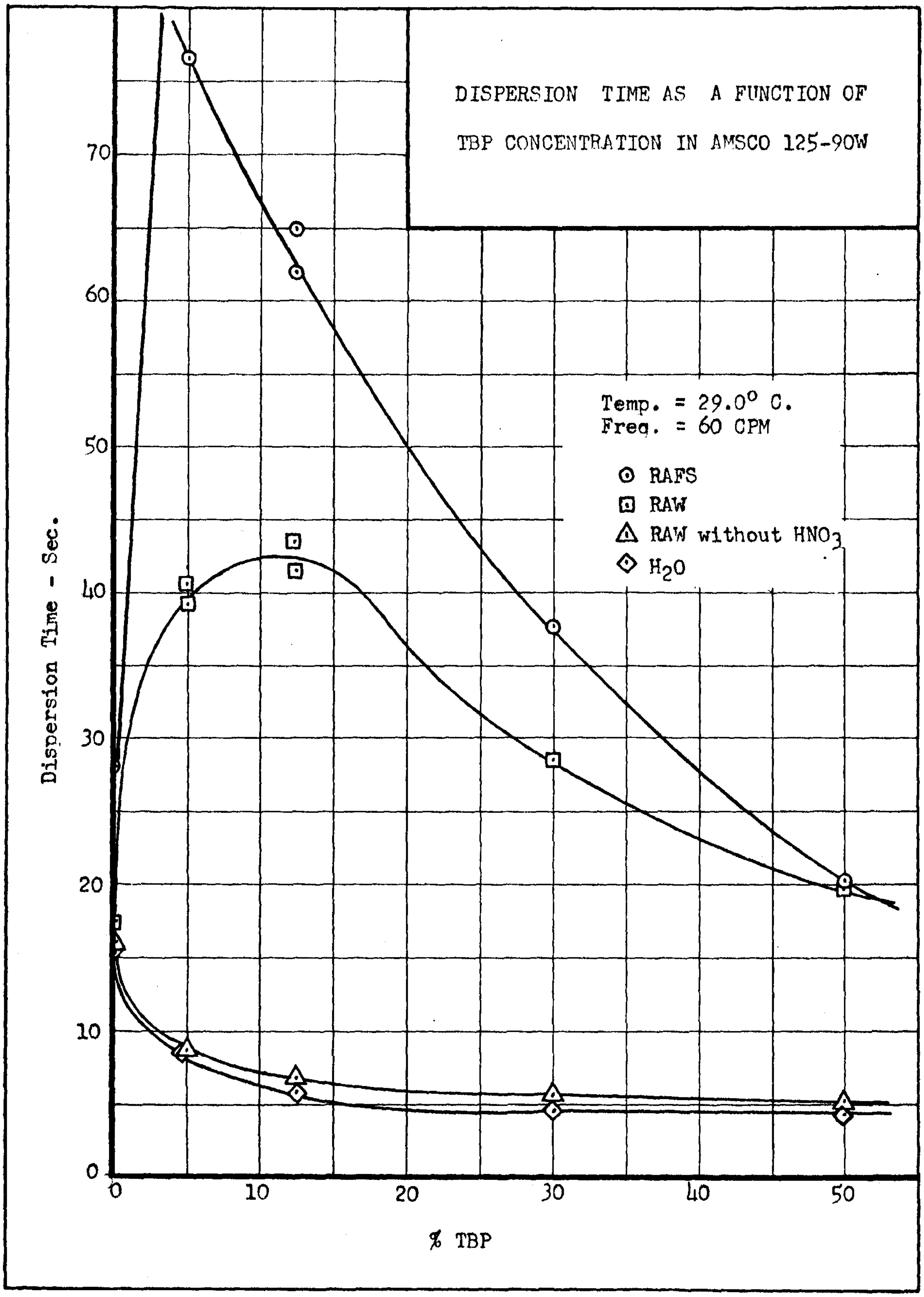
That the stirring frequency has the characteristics of energy is suggested by the observation that if the lowest frequency point is neglected, the dispersion time, Θ, is related to the frequency, δ, by $\Theta = Ae^{-\delta}$ where A is a contant. Figure 12 shows some typical data for 12 1/2% and 30% RAX in contact with RAFS. It may be noted that the temperature data appear to follow an exponential function also. The data are too meager however, to warrant analytical treatment.

4. Solvent Treatment Studies

The previous work employed synthetic solutions made with analytical grade chemicals and re-distilled TBP. Comparison with plant solutions indicate that in general the latter have dispersion time and disengaging time which are 10 to 20% larger. By filtering the solutions, this difference is reduced slightly.

When sodium carbonate wash solutions are used as the aqueous phase, dispersions are rapid but the plant RAX may take two to five times as long to disengage as the synthetic RAX. A few comparisons were made with different aqueous solutions including 0.2% to 10% Na_2CO_3, 0.2% to 10% NaOH and 0.2 to 6% Na_2SO_4. With sodium sulfate solution the disengaging times were not unduly long, about 60-70 seconds, and nearly independent of concentration. With sodium carbonate solutions a minimum disengaging time of 80 seconds was given by the 2% solution and was only slightly greater at higher concentrations. As the concentration is lowered, however, the disengaging time rapidly increases and also the phases do not separate clear. Sodium hydroxide solutions gave a shorter disengaging time than carbonate solutions, and both the disengaging time and the "cleanness" of phases improved as the NaOH concentration increased. These experiments were carried out on only

FIGURE 12


DISPERSION TIME AS A FUNCTION OF
TBP CONCENTRATION IN AMSCO 125-90W
Temp. = 29.0° C.
Freq. = 60 CPM
⊙ RAFS
⊡ RAW
△ RAW without HNO3
◇ H2O
Dispersion Time - Sec.
70
60
50
40
30
20
10
0
0
10
20
30
40
50
% TBP

one sample of plant RAX and may not be typical. If other samples give similar results then it would appear that column tests should be made at different aqueous concentrations.

E. SOLVENT STUDIES (Beatrice R. Jones - L. L. Burger)

In continuing the study of the physical and chemical properties of phosphorus compounds several alkyl phosphate, alkyl phosphonate and alkyl phosphinate esters were investigated with regard to their extraction of plutonium. The compounds which were chosen for this work were, in one case symmetrical with respect to the type of alkyl groups on the molecule: tributyl phosphate, dibutyl butyl phosphonate and butyl dibutyl phosphinate, and in the other case had one small group as has dibutyl methyl phosphate, or had one very large group as has dibutyl decyl phosphate.

Table XXXIII summarizes the data on the extraction of plutonium by the compounds chosen. The esters were dissolved in CCl_4 to a concentration of 0.5 moles/l. except in the case of triphenyl phosphine oxide which was limited by solubility to 0.15 moles/l. As with the extraction of uranyl nitrate, the extraction of both Pu(IV) and Pu(VI) increases with the increasing molecular weight of the esters within each class of compounds. The difference in extraction between members of the same class of compounds is not as great as the increase in extraction between the classes of compounds. While the amount of both uranium and plutonium extracted into the organic increases from phosphates to phosphinates the separation of plutonium from uranium becomes poorer. This latter comparison cannot be considered rigorously however since the compounds are compared under conditions of greatly different concentrations in the organic phase. Table XXXIV lists some of the data for three of the compounds tested. The aqueous systems consisted of 100 g/l UNH and 3 $\underline{M}$ HNO_3 for the uranium data and 100 g/l UNH, 2 $\underline{M}$ HNO_3 and *ca.* 0.95 g/l Pu for each plutonium valence state.

TABLE XXXIII

DISTRIBUTION COEFFICIENTS OF PLUTONIUM WITH 0.5 M PHOSPHATES, PHOSPHONATES, PHOSPHINATES AND PHOSPHINE OXIDES

	Pu III, 5.33×10^7 d/m/ml	Pu IV, 1.27×10^8 d/m/ml			Pu(VI), 1.33×10^8 d/m/ml		
	5 M HNO_3	0.2 M UNH 2 M HNO_3	2 M HNO_3	0.2 M UNH 0.8 M ANN	0.2 M UNH 2 M HNO_3	2 M HNO_3	0.2 M UNH 0.8 M ANN
Dibutyl methyl Phosphate		0.27	0.71	0.39	0.23	0.63	0.52
Tributyl Phosphate	0.0077	0.33	1.57	0.66	0.28	1.09	0.68
Dibutyl decyl Phosphate		0.39	2.26	0.62	0.33	1.65	1.16
Dibutyl methyl Phosphonate		2.12	29.3	6.5	1.05	17.7	6.2
Dibutyl butyl Phosphonate	0.112	3.69	40.1	8.9	1.26	16.2	7.2
Dibutyl decyl Phosphonate		4.39	35.1		1.49	17.7	
Butyl dibutyl Phosphinate	0.153	16.5	171	45.9	5.2	99.3	44.4
Ethyl dihexyl Phosphinate		15.6	206	60.9	12	137	(350)
Triphenyl Phosphine Oxide*	0.048						

*0.15 M since limited solubilty

A C RE

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TABLE XXXIV

EXTRACTION OF URANYL NITRATE, Pu(IV) AND Pu(VI) EXTRACTED AT 24.9°C. BY 0.5 M ESTER IN CCl_4

Compound	% UNH Extracted	% Pu(IV) Extracted	% Pu(VI) Extracted
Tributyl phosphate	77.1	24.7	22.0
Dibutyl butyl phosphonate	92.9	79.1	55.8
Butyl dibutyl phosphinate	99^+	94.5	83.9

It is apparent from Table XXXIII and XXXIV that Pu(IV) extracts from nitric acid solution into the organic phase better than does Pu(VI). On the other-hand, where aluminum nitrate is used as the salting agent the difference in extraction is less apparent and in the case of dibutyl methyl phosphate, dibutyl decyl phosphate and ethyl dihexyl phosphinate, Pu(VI) extracts better than Pu(IV).

V. METAL PRODUCTION STUDIES (W. H. Reas, Problem Leader)

A. ION EXCHANGE COUPLING STUDIES (P. M. Brown)

Further laboratory experiments have been performed to determine the cause or causes of gassing during the elution of plutonium from the resin bed using 6 M HNO_3 - 0.4 M NH_2SO_3H. The laboratory experiments have been performed to determine the effect of such variables as the type of resin, mesh size, and cross-linkag In all cases ca. 20 g of plutonium in 0.3 M HNO_3 - 0.1 M H_2SO_3 were used as the feed solution. The results of these experiments can be summarized as follows:

1. Permutit Q Resin

Eluting Permutit Q resin with 6 M HNO_3 - 0.4 M NH_2SO_3H resulted in sever gassing. The gassing became so rapid during the elution that the resin bed was ruptured. Once the bed had ruptured no further flow of elutriant could be maintained through the columns. The use of Permutit Q resin in this plutonium system is not feasible.

2. Amberlite-IR-112

Previous laboratory experience with Amberlite-IR-112 showed that plutonium could be eluted from the column without gas formation. However, the shrinkage of this resin during the high acid elution cycle is so great that it is very difficult to use a spring and porous plug arrangement to keep the resin in a compact bed. Therefore, a new type of resin column was designed which included a porous plug fixed to the end of a piston which was operated by a hydraulic cylinder. The stroke of the piston was of sufficient length to keep the resin in a compact bed at all times. Unfortunately, the piston and plug assembly was fabricated from a sample of 347 stainless steel which was attacked by the 6 $\underline{M}$ HNO_3 - 0.4 $\underline{M}$ NH_2SO_3H solution, and the corrosion products (presumably iron) catalyzed the oxidation of Pu^{+3} by NO_3^- (or HNO_2) and resulted in extensive gassing of the resin bed. This resin column run was mentioned here to illustrate primarily the effect of stainless steel corrosion products upon resin column operation.

3. Dowex-50, 20-50 Mesh, 8% Cross Linkage

Three resin column runs have been performed with Dowex-50, 20-50 mesh, 8% cross linkage. The elution of plutonium from this resin is characterized by gas-free operation. Very small amounts of gas can be observed, however, if the plutonium is allowed to remain on the resin for a period of 48 to 56 hours prior to the elution operation.

One of the three runs performed was based upon the proposed Recuplex ion-exchange flowsheet. The results of this run are summarized in Table XXXV.

TABLE XXXV

ION EXCHANGE RUN - RECUPLEX OPERATION

Column:	1 1/2" ID x ca. 18" long filled with Dowex-50, 20-50 mesh, 8% cross linkage.
Feed:	3.5 g/l Pu, 0.93 g/l U, 0.3 $\underline{M}$ HNO_3, and 0.1 $\underline{M}$ H_2SO_3 (total feed volume = 6.1 l.); flow = 8 ml/min/cm^2.
Uranium Elutriant:	7.5 liters 0.25 $\underline{M}$ H_2SO_4 (or 21.4 column volumes); flow = 8 ml/min/cm^2.
Elutriant:	6 $\underline{M}$ HNO_3 - 0.4 $\underline{M}$ NH_2SO_3H.
Plutonium Eluate:	477 ml of 35.4 g/l Pu (or 88.5% total Pu removed); uranium content = 1.7 mg U/liter; acidity = 4.77 $\underline{M}$ HNO_3.

It can be seen from Table XXXV that 88.5% of the total plutonium was removed from the resin column at a concentration of 35.4 g/l. Although the plutonium concentration in the eluate is less than 40 g/l, the plutonium band length in the plant column (4" ID) when loaded with 200 g Pu will be greater than the plutonium band length in the laboratory column thus providing for a better elution efficiency. The plutonium concentration in the eluate resulting from plant operation should, therefore, be greater than 40 g/l.

It can also be seen from Table XXXV that the uranium concentration in the plutonium eluate was only 1.7 mg/l U; the column operation thus resulted in a separation factor of ca. 1290.

4. Dowex-50, 50-100 Mesh, 4% Cross Linkage

Approximately 16 g Pu was loaded into a 1 1/2" column containing Dowex-50, 50-100 mesh, 4% cross linkage.. The elution of plutonium from the resin proceeded smoothly and without gas formation. Since the shrinkage of the resin during the elution cycle is about 30%, this run was carried out in the resin column fitted with a porous plug actuated by a hydraulylic cylinder. (The porous plug and piston had been refabricated out of 309 SCb stainless steel. No stainless steel corrosion was observed during the run).

5. Dowex-50, 50-100 Mesh, 8% Cross Linkage

The removal of plutonium from this resin was accomplished with severe gassing resulting from the autocatalytic oxidation of Pu(III) to Pu(IV). A large quantity of iron was found to be initially present in the resin but was removed with 6 M HCl prior to use.

It has been concluded that the cause of the gassing difficulty observed throughout the resin column studies originates from the particular batch of resin used. The standard or commercial grade of Dowex-50 is the 20-50 mesh, 8% cross linkage resin. Since the commercial grade of Dowex-50 is manufactured under controlled conditions to ensure uniformity of product, and since this resin can be used without gassing in plutonium(III) systems, the recommendation is made that the commercial grade of Dowex-50 be used in any plant application. It is further recommended that any batch of resin be tested in a laboratory column before loading a plant column with it.*

B. THE REDUCTION PROCESS - SLAG COMPOSITION INVESTIGATIONS (R. C. Smith, W. B. Tolley)

The equation that represents the reduction of plutonium tetrafluoride to plutonium metal by calcium is as follows:

$$PuF_4 + 2Ca \longrightarrow 2CaF_2 + Pu$$

This reaction is initiated by heating the reactants in a sealed bomb with an electric or an induction heater. It is found, however, that the heat of reaction is not generally sufficient to produce the well shaped button at high yield unless additional heat is supplied to the reactants by means of a "booster". When a booster such as a mixture of calcium metal and iodine is employed, reduction yields of 97-99% are generally obtained. The booster has another function in that it lowers the melting point of the slag, thus providing additional time for the plutonium metal to settle and collect into a single button.

The reduction of plutonium trifluoride by calcium with booster is not as efficient as the reduction of plutonium tetrafluoride under the same conditions. Since this laboratory has shown that plutonium trifluoride can be prepared by the reaction of Freon-12 with plutonium oxalate at elevated temperatures, thus possibly eliminating the use of hydrofluoric acid in 234-5 operations, it becomes important to be able to reduce plutonium trifluoride to the metal with good yield and purity. Laboratory work, therefore, has been undertaken to determine operating conditions which will permit the reduction of plutonium trifluoride to the metal with high yield and purity.

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*Since writing this report, other experiments have been performed with different batches of Dowex-50, 20-50 mesh, 8% cross linkage. Since some of these runs were accompanied with gassing during the elution cycle, the need for testing a resin batch before installation in a plant column is further borne out.

At the present time cerium trifluoride is being used as a stand-in for plutonium trifluoride. The reduction of cerium trifluoride by calcium has been performed with various quantities of booster present. The resulting slags have varied in composition from 80 mol % calcium fluoride to 40 mol % calcium fluoride. Concurrently the melting point of slags of various composition have been determined by thermal analysis of calcium fluoride-calcium iodide mixtures. The data obtained in these investigations are presented in Tables XXXVI and XXXVII.

TABLE XXXVI

REDUCTION OF CeF_3 BY CALCIUM USING VARIOUS AMOUNTS OF BOOSTER

Run	% Ce Yield	% CaF_2 in Slag	Slag Melting Point, °C.
1	65	79	1215
2	65	79	1215
3	57	79	1215
4	92	50	995
5	94	50	995
6	96(a)	50	995
7	89	40	908
8	72(a)	40	908
9	83	40	908
10	97	40	908

(a) The bomb developed a leak during firing.

It can be seen in Table XXXVI that reduction yields of about 95% are obtained when the resulting slag is 50 mol % calcium fluoride. In all of the reductions performed a 33% excess of calcium over the theoretical amount required by the reaction was used. The metal yields of reduction which produce a slag containing about 40 mol % calcium fluoride scatter from 83 to 97%. Additional runs at the same conditions are contemplated to determine more precisely the average reduction yield.

The data of Table XXXVII show that the eutectic composition of the calcium iodide-calcium fluoride system is about 18-19 mol% calcium fluoride. The melting point of the eutectic mixture is about 660°C. A large number of runs have been performed at compositions below 18 mol % calcium fluoride, however, this region of the com-

TABLE XXXVII

Temperature Composition Diagram of the
System: $CaF_2 - CaI_2$

Mol % CaF_2	Break °C.	Halt °C.
100	1360[(a)]	---
90	1295[(b)]	---
80	1227[(b)]	---
70	1158[(b)]	---
60	1080[(b)]	---
50	995[(b)]	---
42.3	932	665
32.7	840	658
24.7	745	670
22.0	760	660
21.6	773	663
21.6	700	650
21.1	---	655
20.5	685	612
19.8	680	665
18.8	(665)	657
0.00	740	---

(a) Melting point taken from literature.
(b) Break temperatures estimated by graphical interpolation.

position diagram appears to be complex. It is hoped that refinement of laboratory technique and equipment will permit the determination of phase equilibria in the region of 0-18 mol % calcium fluoride.

VI. RUTHENIUM CHEMISTRY (A. S. Wilson, Problem Leader)

A. THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY RUTHENIUM(IV) PERCHLORATE SOLUTIONS (A. S. Wilson)

The investigation of this reaction has been extended to conditions where the initial concentration of hydrogen peroxide is between three and five molar. Observational differences between these experiments and previously reported experiments[1] are immediately apparent. The ruthenium changes its species quite quickly (ca. one-half hour) as evidenced by the color changes in the solution. In addition the rate of decomposition of the hydrogen peroxide is no longer first

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[1] HW-26104, Quarterly Report, July through September, 1952, Chemical Research, Page 97.

order in hydrogen peroxide. Preliminary results indicate that the data cannot be explained by a rate law which contains only one term. Moreover, additonal experiments in systems in which the hydrogen peroxide is initially tenth molar indicate that at acid concentrations below tenth molar the rate law,

$$-d(H_2O_2)/dt = k(H_2O_2)(Ru^{IV}_T)(H^+_T)^\circ,$$

is no longer valid.

B. RUTHENIUM(IV) CHLORIDE COMPLEXES (J. L. Swanson)

This system is being investigated spectrophotometrically. Preliminary results indicate that the chloride complexes are mononuclear as has been proposed[1]. This observation is based on a study of two solutions with different total ruthenium (IV) concentrations, 1.02×10^{-3} M and 5.10×10^{-4} M, but identical in other constituents; 1.0 M $HClO_4$, 4.0 M $NaClO_4$ and 1.0 M NaCl, which were allowed to come to equilibrium at 64°C. The criterion for equilibrium was the observation of essentially no change (2%) in the spectrum at 454 mu and 385 mu between the first and fourth days. The measured molar extinction coefficients were independent of ruthenium(IV) concentration. This result shows that an interpretation of present and future spectrophotometric data may be made using the idea of corresponding solutions[2], since one requirement of this method is that the complexes to be studied be mononuclear.

VII. WASTE TREATMENT (R. E. Burns, Problem Leader)

A. EFFECT OF DECONTAMINATING AGENTS ON $BiPO_4$ WASTE SYSTEM (C. R. McMullen)

Some work concerning the effect of cleaning agents, proposed for decontamination of process equipment and cell walls in the $BiPO_4$ process canyons, on the behavior of fission products and plutonium during residence in the waste settling tanks and on subsequent discharge to ground have already been reported[3]. These studies were made in support of a test program for decontamination of two cells in the B canyon. The investigations have been extended to include some

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1. P. Wehner, and J. C. Hindman, J. Phys.Chem., 56 10 (1952).
2. J. Bjerrum, Kgl, Danske Vindenskak, Selskab, Math. - fys. Medd. 21 No. 4 (1944).
3. HW-25166, Quarterly Report, April through June, 1952, Chemical Research, Page 75.

cleaning agents not included in the previous studies and under conditions more nearly approximating those expected when processing operations in the canyon have ceased.

Table XXXVIII shows the results of a series of experiments made to determine whether or not cleaning agents proposed for decontamination interfere with adsorption by soil of radioactive components present in supernatant from the 110-111-112 B settling tank cascade. Equal volumes of 112B supernatant and the cleaning solution were mixed. Twenty ml of the mixture was stirred for one hour with one gram of "soil". "Soil" refers to a composite prepared by mixing equal weights of soil from the 20, 30, 40 and 50 foot levels from Well 224-B-3. Particles larger than 28 mesh were discarded.

Table XXXIX shows the results of a series of experiments designed to determine the tendency of the various cleaning solutions to remove radioactive elements already adsorbed on soil. Several one-gram samples of the soil were contacted serially with two ten-milliliter portions of 112B supernatant and then washed with a 10 ml portion of water. Radioactive content of the soil was determined by measuring the difference in radioactive content of the solutions before and after contacting with the soil. The contaminated soil was then stirred for 30 minutes with a 10 ml portion of cleaning solution. Slurry was allowed to stand one hour and was then centrifuged. Gross beta and plutonium were determined for the supernatant.

Data presented in Table XXXVIII show that, of the cleaning agents tried, only Hilco had any detrimental effect on adsorption of fission products by soil. Hilco also showed greater tendency to prevent adsorption of plutonium on soil than the other cleaning agents tried. Because the total plutonium count in the supernatants obtained in these experiments was very low, accuracy obtained was

TABLE XXXVIII

EFFECT OF CLEANING AGENTS ON ADSORPTION OF RADIOACTIVE ELEMENTS BY SOIL

Equal Volumes Cleaning Solutions and 112B Supernatant

Soil: Composite of Equal Weights from 20, 30, 40, 50 ft. levels. 224-B-3 Well.

20 ml Solution Stirred One Hour with 1 g. Soil

Cleaning Solution	Gross β Activity Remaining in Supernatant, %	Pu Remaining in Supernatant, %
5% NaOH*	49	29
1% Versene, 5% NaOH	52	34
1% Sodium Citrate, 5% NaOH	51	17
1% Na_3PO_4, 5% NaOH	50	2.9
1% H_3BO_4, 5% NaOH	50	43
1% NH_4HF_2, 5% NaOH	52	11
1% $Na_2Cr_2O_7$, 5% NaOH	51	11
1% $Na_2C_2O_4$, 5% NaOH	51	5.6
1% $(NH_4)_2SiF_6$, 5% NaOH	50.5	5.6
1% Sodium Tartrate, 5% NaOH	52	11
2.5% Hilco, 0.5% Na_2CO_3	60	85
None*	66	13

*Control experiments

TABLE XXXIX

REMOVAL OF RADIOACTIVE ELEMENTS FROM SOIL BY CLEANING AGENTS

1 gm contaminated soil stirred 30 min. with 10 ml cleaning solution. Soil contained 1.74×10^4 β c/m (7.5% Geom.) and 780 c/m (50%) Pu.

Cleaning Solution	β Activity Removed, %	Pu Removed, %
5% NaOH	5.7	2.5
1% Versene, 5% NaOH	16	1.9
1% Sodium Citrate, 5% NaOH	6.9	2.2
1% Na_3PO_4, 5% NaOH	5.9	1.0
1% H_3BO_4, 5% NaOH	6.6	1.3
1% NH_4HF_2, 5% NaOH	5.9	1.6
1% $Na_2Cr_2O_7$, 5% NaOH	6.7	0.3
1% $Na_2C_2O_4$, 5% NaOH	6.7	0.3
1% $(NH_4)_2SiF_6$, 5% NaOH	6.3	1.0
1% Sodium Tartrate, 5% NaOH	16	7.6
2.5% Hilco, 0.5% Na_2CO_3	7.0	2.5
Simulated 112 Supernatant Without Radioactive Const.*	6.4	20 **

* Control experiment

** Plutonium counts in supernatant so low that accuracy of this number is doubtful.

low and it is doubtful that the apparently poorer plutonium adsorption in the presence of boric acid is significant. Data presented in Table XXXIX indicate that only Versene and tartrate increase the desorption of fission products over that obtained with five per cent NaOH or 112 supernatant. Plutonium desorption was increased significantly only by tartrate.

From these data it appears that Versene, tartrate and Hilco are the only cleaning agents, among those studied, which have any adverse effect on adsorption of fission products and plutonium by soils. They should be used only if necessary and as sparingly as possible.

Another series of experiments was performed to determine how well fission products and plutonium are carried by ferric hydroxide from solutions containing some of the cleaning agents mentioned above. In the event that some batches of cleaning solutions have, after use, such high activity that discharge of them to the settling tanks is questionable, some scavenging of them may be desirable. Table XL shows the results of these experiments. In each, a 20 ml portion of the cleaning solution was spiked with dissolver solution, brought to pH 3 with HNO_3 and made 0.01 $\underline{M}$ in $Fe(NO_3)_3$. While stirring, NaOH was added to raise the pH to 10 or greater. The resulting ferric hydroxide precipitate was removed by centrifugation and plutonium and beta analyses were made on the supernatants.

Versene and tartrate exert a detrimental effect on the carrying of both fission products and plutonium. Fission product and plutonium decontamination factors of about 20 and 100 respectively were obtained for the other cleaning solutions studied. In practice, the ferric hydroxide slurry would be jetted to the settling tanks rather than centrifuged.

B. <u>SOLVENT EXTRACTION OF FISSION PRODUCTS</u> (C. R. McMullen)

It has been reported by Baldwin, W. H. and Higgins, C. E.[1] that certain organo-phosphorus compounds, and particularly dibutyl phosphine oxide, when dis-

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[1] Baldwin, W.H. and Higgins, C.E., ORNL-1338, Organo-Phosphorus Compound For Solvent Extraction, August 14, 1952.

TABLE XL

CARRYING OF PLUTONIUM AND FISSION PRODUCTS BY FERRIC HYDROXIDE PRECIPITATED IN CLEANING SOLUTIONS

Cleaning Solution*	Gross β D.F.	Pu D.F.
1% Citric Acid, 5% NaOH	20	330
1% Na_3PO_4, 5% NaOH	18	66
1% $Na_2C_2O_4$, 5% NaOH	20	104
1% Tartaric Acid, 5% NaOH	4.2	8.7
1% Versene, 5% NaOH	11.	27
2.5% Hilco, 0.5% Na_2CO_3	8	104

*Cleaning solution spiked to contain ca. 40,000 β c/m/ml (2nd shelf) and 165 Pu c/m/ml (50% Geom.). Solutions brought to pH 3 with HNO_3, $Fe(NO_3)_3$ added to 0.01 M, NaOH added to pH 10 or greater.

solved in carbon tetrachloride extract appreciable amounts of fission products from nitric acid solution. Further studies of the extraction of fission products by a tributyl phosphine oxide-carbon tetrachloride solvent (hereafter written as TBPO-CCl_4) are in progress for the purpose of determining the applicability of the procedure to the recovery of zirconium and niobium from process wastes.

Table XLI shows distribution ratios, E_a°, obtained for various fission products when equal volumes of 0.1 M TBPO in CCl_4 and nitric acid solutions containing Hanford dissolver solution were contacted. These data show that TBPO-CCl_4 as a solvent extracts essentially only zirconium and niobium among the fission products present in aqueous solution and that extraction of zirconium and niobium is increased by nitric acid as a salting agent without a coincident increase in extraction of other fission products.

These data were, in general, confirmed by contacting 0.1 M TBPO-CCl_4 with an equal volume of 1 M HNO_3 containing a specific fission product as tracer. In these experiments, E_a°'s of 6.7, 0.015, 0.0087 and 0.16 were obtained for Zr^{95}-Nb^{95}, Sr^{90}-Y^{90}, Cs^{137} and Pm^{147}, respectively.

Table XLII shows the distribution ratios obtained by successively contacting a Zr^{95}-Nb^{95} spiked nitric acid solution with equal volume portions of

TABLE XLI

DISTRIBUTION OF FISSION PRODUCTS BETWEEN NITRIC ACID SOLUTION AND TRIBUTYLPHOSPHINE OXIDE-CARBON TETRACHLORIDE SOLVENT

Aqueous Phase: Spiked with dissolver solution (300 days old) to about 10^6 β c/m/ml (7.5% Geom.).

Organic Phase: 0.1 M TBPO in CCl_4.

Equal Volumes Aqueous and Organic Phases Contacted 30 Minutes.

Activity	Distribution Ratios E_a^o		
	Aqueous 5 M HNO_3	Aqueous 1 M HNO_3	Aqueous 0 M HNO_3
Gross β	0.1	0.04	0.17
Gross γ	4.7	1.1	1.7
Cs	0.003		0.007
Zr	Large*		0.39
Nb	Large*		16.
Ce	0.01		0.04
Total R.E.	0.0004		0.0006
Sr	0.001		0.004
Ru	0.0006		0.012

*Activity remaining in aqueous too low for accurate measurement.

TABLE XLII

EXTRACTION OF Zr^{95}-Nb^{95} TRACER FROM NITRIC ACID SOLUTION BY TBPO-CCl_4

Activity Initially Present In Aqueous, c/m/ml*	Distribution Ratios, E_a^o				Activity In Aqueous After 3 Extractions, %
	HNO_3 In Aqueous M	1st Extn.	2nd Extn.	3rd Extn.	
5.4×10^6	1.0	6.7	2.3	2.8	0.6
4.4×10^5	2.2	2.53	1.31	1.02	6.
1.7×10^5	2.2	2.3	0.93	0.76	8

*As measured by a gamma scintillation counter at about 8% geometry.

0.1 M TBPO-CCl_4 extractant. Although no explanation for the variation in observed E_a°'s is immediately apparent, it does appear that essentially complete extraction of zirconium and niobium can be accomplished with a small number of extraction stages.

Table XLIII shows the results of a series of experiments on removal of zirconium and niobium from a TBPO-CCl_4 phase by various stripping agents. Water was not at all effective in stripping zirconium and niobium from the organic phase. Hydrofluoric acid is an effective stripping agent in that better than 99% of the activity was removed in two strip stages under the conditions used.

Distribution ratios for the extraction of plutonium in various oxidation states from nitric acid solutions into 0.1 M TBPO-CCl_4 were measured. An E_a° of 0.4 was found for Pu(III) between the solvent and an aqueous phase containing 1.8 M HNO_3, 0.7 M $H_2NOHHCl$ and ca. 70,000 d/m/ml Pu. It was not shown that plutonium in the organic phase was Pu(III). An E_a° of 160 for Pu(IV) was obtained when the solvent was contacted with an aqueous phase containing 2.5 M HNO_3 and ca. 1.3×10^5 d/m/ml Pu(IV) and an E_a° of 29 for Pu(VI) when the aqueous phase was 2.5 M in HNO_3 and contained ca. 3×10^4 d/m/ml Pu(VI). When the organic phases obtained in the above extraction of Pu(IV) and Pu(VI) were stripped with equal volumes of 0.01 M HF, distribution ratios of 0.7 and 24.8 (E_a°) were obtained for Pu(IV) and Pu(VI) respectively.

Further studies of this system will be made to better define the fission product extraction, the degree of plutonium interference and ways to avoid it and to explore the application of the system to actual waste streams.

C. IODINE IN PUREX SOLVENT (W. E. Clifford)

Iodine present in Purex process feed solution (HAF) is readily extracted by TBP-diluent solvents. Once extracted, the iodine is difficult to remove from the organic phase, only a small part being removed during the stripping of uranium

TABLE XLIII

REMOVAL OF Zr AND Nb FROM TBPO-CCl_4 BY STRIPPING

0.1 M TBPO-CCl_4 containing Zr^{95}-Nb^{95} tracer contacted with an equal volume of stripping agent.

Stripping Agent	Zr^{95}-Nb^{95} Activity In Original Organic, c/m/ml*	Distribution Ratios E_a° 1st Strip	2nd Strip	3rd Strip
Water	4.7×10^6	1,000		
0.01 M $H_2C_2O_4$	4.7×10^6	0.34	0.22	7.1
0.01 M HF	1.3×10^5	0.21	0.039	
0.01 M HF	3.5×10^5	0.31	0.048	0.043

*As measured by a gamma scintillation counter at about 8% geometry.

or plutonium. The solvent recovery procedure presently considered for the Hanford Purex process, a sodium carbonate wash followed by two water washes, does not remove iodine completely from contaminated solvent. Under these circumstances appreciable amounts of iodine may be recycled with the solvent. When processing uranium cooled at least 90 days the possible build-up of active iodine in the organic phase due to this recycle would not be serious. With shorter cooled uranium such recycle of active iodine could make direct maintenance of the solvent recovery system impossible. These studies were made in an effort to determine something of the manner in which iodine is held in the TBP-solvent phase and to investigate alternate solvent washing techniques from the standpoint of iodine decontamination.

Table XLIV shows the distribution of iodine throughout extraction and strip solutions obtained in the preparation of a synthetic IOF solution. Synthetic HAFS, spiked with inert and radioactive iodine, was extracted once with HAX. The resulting organic phase was scrubbed twice with HAS, stripped six times with HCX and then diluted with 1.3 volumes of organic phase of ICW composition to produce

TABLE XLIV

DISTRIBUTION OF IODINE IN PUREX STREAMS

Stream	Iodine, %
HAFS (Starting Soln)	100
HAW (Aqueous After Extn.)	11
1st Scrub	1.1
2nd Scrub	0.87
HAP (Scrubbed Organic)	87.
1st Strip	0.49
2nd Strip	0.43
3rd Strip	0.34
4th Strip	0.33
5th Strip	0.31
6th Strip	0.31
HCW (Stripped Organic)	85.

TABLE XLV

IODINE REMOVAL WITH VARIOUS WASHING PROCEDURES

Expt. No.	Age of IOF	Aqueous Composition	Volume Ratio O/A	Contact Time	Iodine Removed, %
1	---	1 $\underline{M}$ Na_2CO_3	6.7	3 min.	3
2	5 days	1 $\underline{M}$ Na_2CO_3	6.7	2 hrs.	12
3	---	1 $\underline{M}$ Na_2CO_3	10	1.5 min.	1.1
4	---	1 $\underline{M}$ Na_2CO_3	10	16 hrs.	18
5	1 day	0.5 $\underline{M}$ NaOH, 0.5 $\underline{M}$ Na_2CO_3	5	6 min.	38
6	6 days	" " " "	5	6 min.	44
7	---	" " " "	10	1.5 min.	1.8
8	8 days	5 $\underline{M}$ KOH	3	3.5 hrs.	85
9(a)	8 days	Water	1	3 min.	3
10	9 days	5 $\underline{M}$ KOH	2	73 hrs.	93
11	2 days	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ Na_2CO_3	3	5 min.	11
12	6 days	" " " "	3	5 min.	20
13(b)	6 days	" " " "	2.5	17 hrs.	15
14	7 days	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ NaOH	2.5	1.3 hrs.	4
15	30 min.	0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3	1	16 min.	44
16	---	0.8 $\underline{M}$ H_2O_2, 0.5 $\underline{M}$ NaOH	10	1.5 min.	1.5
17	---	Solid $NaBiO_3$, 1 $\underline{M}$ Na_2CO_3	10	1.5 min.	0.7
18	---	0.1 $\underline{M}$ $Hg(HO_3)_2$	10	1.5 min.	1.0
19(c)	5 days	0.1 $\underline{M}$ $Hg(NO_3)_2$, 0.5 $\underline{M}$ HNO_3	2.8	15 min.	3
20	---	Soluble Starch Soln.	4.3	1.5 min.	0.0

(a) Organic from Expt. 8
(b) Organic from Expt. 3
(c) Organic from Expt. 2

synthetic IOF. The results obtained confirm previously reported data in that most of the iodine entering the Purex process in feed solution will leave the extraction system in the organic streams.

A series of batch contacting experiments employing synthetic IOF (preparation just described) and various wash solutions was performed to study iodine decontamination as a function of washing conditions. Pertinent information and results obtained in these experiments are shown in Table XLV.

It is apparent from Experiments 2 through 4, Table XLV that sodium carbonate washing removes only a small part of the iodine present in the organic phase. Increasing the alkalinity of the wash appears to increase iodine removal somewhat (Expts. 5, 6, 7) although prolonged contact with strong caustic failed to remove all of the iodine (Expts. 8 and 10). Including reducing agents (Expts. 11 to 15), oxidizing agents (Expts. 16 and 17) or possible complexing agents for iodine (Expts. 18 to 20) failed to produce any significant improvement in iodine removal except in the case of sodium sulfite as a reducing agent (Expt. 15).

In an attempt to determine how iodine is extracted into TBP-diluent mixtures either an aqueous solution of inert iodine or solid compounds of iodine (in several oxidation states) was contacted with TBP, diluent or TBP-diluent phases. Spectrophotometric studies and chemical analyses were employed to follow iodine during the experiments. Observations made and tentative conclusions reached were as follows.

1. TBP dissolves I_2, KI and HI but will not dissolve iodate compounds.
2. Amsco 125-90W, the diluent used in these studies dissolves I_2 but not compounds of iodide or iodate.
3. TBP-Amsco 125-90W shows all of the solution properties toward iodine compounds characteristic of either component separately.
4. Amsco 125-90W reacts with iodine to form iodo-organic compounds. This reaction is relatively slow but iodine so combined is very difficult to remove by washing procedures. Reaction is probably an iodination of olefinic bonds present to a small extent in Amsco 125-90W.

5. Iodide dissolved in (not reacted with) TBP-Amsco 125-90W is readily removed by water or alkaline aqueous washes.

6. TBP appears to complex iodine in some oxidation state above zero, perhaps +1. Evidence for this conclusion was derived from spectrophotometric studies of a TBP-Amsco 125 phase containing I_2 and treated with caustic or caustic carbonate scrub. The shape of the absorption curve was changed and became, in some places, even higher than before the alkali treatment. On standing, color attributable to I_2 and removable by alkaline scrub grew into the scrubbed organic phase.

Iodine which has combined with unsaturated constituents of Amsco 125-90W is very difficult to remove from the solvent phase. Some experiments were done to determine whether or not radioactive iodine so held could be removed by exchange with inert iodine. Synthetic IOF containing radioactive iodine was contacted with aqueous inert KI-I_2 solution prior to washing. Results of these experiments are shown in Table XLVI (Expts. 1a to 3a). Comparison with Expt. 15, Table XLV shows that considerable improvement in radioactive iodine removal was obtained.

Also shown in Table XLVI are the results of experiments in which an attempt was made to saturate olefinic bonds present in the Amsco-125 prior to use of the diluent for preparation of synthetic IOF. The solvent, TBP-Amsco 125, was contacted with an aqueous KI-I_2 solution in order to iodinate the unsaturates. In the (b) experiments shown, excess iodine was removed from the solvent by contact with a 0.1 M Na_2SO_3, 1 M Na_2CO_3 solution; in the (c) experiments excess iodine was not removed.

Some improvement in iodine decontamination during solvent washing was observed in the experiments in which excess iodine was removed, particularly when the wash solution contained sulfite. A greater improvement was observed when excess iodine was left in the solvent. Again, best results were obtained when the wash solution contained a reducing agent.

Recent design specifications for the Purex plant include the solvent washing facilities in a remote maintenance area. Because of these design changes

TABLE XLVI

REMOVAL OF RADIOACTIVE IODINE FROM SOLVENT TREATED WITH INERT IODINE

Expt. No.	Age of IOF	Aqueous Composition	Volume Ratio O/A	Contact Time	Iodine Removed, %
1a(1)	40 min.	0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3	1	16 min.	84
2a	3.5 hrs.	" " " "	1	15 min.	74
3a(2)	3.5 hrs.	" " " "	1	10 min.	30
1b(3)	2 hrs.	1 $\underline{M}$ NaOH	1	10 min.	38
2b	1.5 hrs.	1 $\underline{M}$ NaOH	1	35 min.	32
3b	25 min.	0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3	1	30 min.	89
4b(4)	25 min.	1 $\underline{M}$ NaOH	1	30 min.	45
5b	5 hrs.	0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3	4.2	40 min.	33
6b	1.5 hrs.		4.2	5 min.	25
7b	4 hrs.	0.14 $\underline{M}$ NH_2OH, 1 $\underline{M}$ Na_2CO_3	1	16 min.	21
8b	28 min.	" " " "	4.5	5 min.	10
9b	4 hrs.	" " " "	4.2	16 min.	12
10b	28 min.	" " " "	4.5	35 min.	18
11b	4 hrs.	" " " "	4.2	35 min.	20
12b	4 hrs.	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ NH_3	1	16 min.	31
1c(5)	3 hrs.	1 $\underline{M}$ Na_2CO_3	1	10 min.	46
2c	30 min.	0.5 $\underline{M}$ Na_2CO_3, 0.5 $\underline{M}$ NaOH	1	3 min.	57
3c	1 day	" " " "	1	2.75 hrs.	45
4c	1 day	" " " "	1	20 hrs.	61
5c	15 min.	0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3	1	30 min.	96
6c	2.5 hrs.	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ Na_2CO_3	1	3 min.	57
7c	2 days	" " " "	1	50 min.	77
8c(6)	2 days	Water	1	3 min.	0
9c	2 days	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ Na_2CO_3	1	18 hrs.	77
10c(7)	2 days	Water	1	5 min.	0
11c	1 day	0.09 $\underline{M}$ NH_2OH, 1 $\underline{M}$ NH_3	1	6 min.	87

(1) In the (a) experiments the prepared synthetic IOF containing active iodine was contacted with an aqueous $KI-I_2$ solution prior to scrubbing.

(2) Organic from Expt. 2a.

(3) In the (b) experiments, the solvent, TBP+Amsco 125-90W was contacted with aqueous $KI-I_2$ solution and the excess iodine was removed by contact with 0.1 $\underline{M}$ Na_2SO_3, 1 $\underline{M}$ Na_2CO_3 solution before the solvent was used to prepare synthetic IOF.

(4) Organic from Expt. 3b.

(5) In the (c) experiments the solvent, TBP-Amsco 125-90W was contacted with aqueous $KI-I_2$ solution prior to use in preparation of synthetic IOF. Excess iodine was not removed.

(6) Organic from Expt. 7c.

(7) Organic from Expt. 9c.

immediate interest in the problem of radioactive iodine in solvent has greatly decreased. Consequently, no further work on the problem is planned at this time.

D. EMULSIONS AND SOLIDS FORMED IN PUREX SOLVENT RECOVERY (R. I. Miller)

In some Purex Process pilot plant runs made at ORNL, solids-stabilized emulsions were formed during carbonate washing of the solvent (30% TBP-Amsco). These emulsions were carried over into the solvent receiving tanks, where complete separation of the phases required days. In addition to the solids-stabilized emulsions, the organic phase was cloudy due to suspended droplets of aqueous phase, which cloudiness also persisted for several days. Both the suspended aqueous phase and the solid material were high in radioactive constituents.

These problems were considered of sufficient importance that several research groups at Hanford were asked to cooperate in working on them. Among other things, Chemical Research was asked to study the possibility that impurities in the carbonate wash solution were responsible for the formation of solids when contacted with solvent. These studies were to involve only non-radioactive solvent.

A large number of batch contacts were made between 1 $\underline{M}$ Na_2CO_3 wash solutions prepared from sodium carbonate obtained from several different sources and solvents prepared from Amsco-125-90W and TBP obtained from various sources. Carbonates used included Baker and Adamson, A.C.S. Specifications material obtained from the stock room, technical grade from Building 321, technical grade from Building 271T, Baker's Analyzed Reagent Grade from ORNL and technical grade (Mathieson) from ORNL. The latter two materials have been used in pilot plant runs at ORNL. Samples of TBP used in the preparation of solvent included highly purified (vacuum distilled) TBP and TBP as received from the supplier. Also, solvent which had been used in cold Metal Recovery and Purex runs in the 321 building was used. In these contactings, the ratio of organic to aqueous was five and the total volume of both phases was about 100 ml. Solvent was 30% TBP-Amsco 125-90W.

Although in almost all cases the organic phase was cloudy after contact with the carbonate, in no case was a stabilized emulsion or any large amount of solid formed. The organic phase could be cleared by a minimum of centrifuging ($<$ 5 min. at 700 G.).

Similar batch contact experiments were performed in which the organic phase was made 0.008 M in uranium and spiked with 500 ppm. of TBP hydrolysis products - dibutyl phosphate, monobutyl phosphate and phosphoric acid. Neither stable emulsion nor appreciable solid formation was observed in any of the experiments whether the hydrolysis products were present singly or in combination. In one experiment in which solvent containing vacuum distilled TBP, 0.008 M uranium and 12,000 ppm. of MBP was contacted with 1 M Na_2CO_3, technical grade from the 271 building, the washed solvent remained hazy even after long standing. In a similar experiment the solvent contained "as received" TBP, 0.008 M uranium and 4000 ppm. of DBP. Some solid was present at the interface and phase separation was slow.

Spectrographic analyses for impurities were obtained on Baker and Adamson A.C.S. Specifications sodium carbonate and on technical grade sodium carbonate from Building 271T and from ORNL. Traces of Mg and Si were reported in all three samples. Traces of Cu, Fe and B and trace to medium Ca was reported for the Building 271T technical carbonate. No other elements except sodium were detected in any of the samples.

These experiments indicate that the impurities present in the carbonates used are not directly responsible for the formation of solids or stabilized emulsions in the Purex solvent washing procedure. They do not exclude the possibility that impurities present in these carbonates might form solids on contact with solvent containing fission products or decomposition products caused by irradiation of the solvent.

VIII. DOCUMENTED REPORTS ISSUED DURING QUARTER, OCTOBER THROUGH DECEMBER, 1952

Document No.	Date of Document	Author(s)	Title
HW-25756	9-29-52	C. Groot	Report of Trip to Oak Ridge 9-11-52.
HW-25757	10-17-52	C. Groot	The Volatile Fluoride Processes, Status as of September 9, 1952.
HW-25780	8-20-52	H. C. Carney	Visit to California Radiation Laboratory and Livermore Project, August 4, 1952.
HW-25911	10-13-52	H. H. Hopkins E. E. Voiland	Preliminary Metal Ion Distribution Study in Redox and Uranium Recovery Process Systems.
HW-26022	10-22-52	L. L. Burger W. E. Roake	Report of Invention "The Preparation of Plutonium Trifluoride for Reduction to Metal by Means of a Solid Phase - Gas Reaction between Plutonium Compounds and Freons.
HW-26027	10-23-52	W. W. Schulz R. A. Watts R. L. Moore	Report of Invention "Decontamination of Redox and Purex Streams by Adsorption of Ruthenium-Organo Sulfur Complexes on Adsorption Columns.
HW-26028	10-23-52	W. S. Figg O. H. Koski D. C. Kaulitz	Report of Invention "A Remotely Driven, Smooth Flow, Adjustable Rate, Positive Displacement Pump."
HW-26104	11-3-52	O. F. Hill	Quarterly Report, July Through September, 1952.
HW-26458	11-17-52	A. S. Wilson	Report of Invention "The Use of H_2O_2 to Improve the Decontamination in Solvent Extraction Processes."
HW-26484	12-2-52	C.R.McMullen R E. Burns	Effect of Decontamination Agents on Adsorption of Fission Products and Plutonium by Soil.
HW-26517	12-5-52	R. M. Wagner	Nitration Reactions of Shell Spray Base Under Purex Waste Recovery Process Conditions.
HW-26531	12-10-52	R. L. Moore R. A. Watts	Production of UO_3 by Calcination of Uranyl Peroxide.

IX. ABSTRACT

Progress is reported on the work performed during the quarter by Chemical Research, Separations Technology Unit. The report covers process work performed on the Uranium Recovery Process, distribution of metal-ion impurities (in both the Redox and Uranium Recovery Processes), a second plutonium cycle for the Purex Process using reflux to obtain added decontamination and a concentrated product, and the Recuplex Process. Process improvement studies are reported on the effect of dissolving conditions on fission-product behavior during solvent extraction, extraction from hydrochloric acid solutions, scavenging ruthenium activity with mercaptans, production of UO_3 by calcining uranyl peroxide, and nitric acid recovery. Physical chemistry studies of solvent extraction included activity coefficients of TBP, solubility of TBP in water from various TBP-diluent solutions, self-diffusion of TBP, liquid-liquid dispersion studies and organophosphorus solvent studies. Ion exchange coupling investigations are reported. The effect of slag composition on reduction yields are given. Progress on fundamental ruthenium chemistry is reported. Waste treatment investigations included effect of decontaminating agents on the $BiPO_4$ waste systems, solvent extraction of fission products, behavior of iodine in the Purex solvent and studies of emulsions and solids formed in Purex solvent recovery.

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